# EFFECT OF SOIL TYPE AND FERTILIZER APPLICATION TIMING ON PHOSPHORUS LEACHING FROM GYPSUM-TREATED AGRICULUTRAL SOILS

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Phosphorus is an essential plant nutrient and an important contributor to the eutrophication of aquatic ecosystems. Studies have shown that gypsum ($CaSO_4 \cdot H_2O$) applications can potentially reduce phosphorus export from agricultural fields. Most studies have examined the effect of gypsum application rates on treatment effectiveness, but limited research has been conducted to determine how the timing of gypsum application can affect soil phosphorus mobility and phosphorus leaching. A greenhouse experiment was conducted to address this question and further our understanding of the effect of gypsum addition on soil phosphorus chemistry. For the experiment, two soil types with different background phosphorus levels (low P, high P), and three different time intervals between gypsum and phosphorus fertilizer application (2, 28 and 56 days) were applied. A total of 18 soil columns (L: 15 cm; diam: 10 cm) packed with sieved soil were treated with gypsum (3.9 g) and separated into three sets corresponding to each of the phosphorus application times. An equal number of columns not treated with gypsum were also included to serve as controls. Phosphorus fertilizer (0.34 mg P $cm^{-1}$) was added as $KH_2PO_4$ solution. Rainwater (58 mL) was applied every 2-4 days to generate leachate that was collected and analyzed for ortho-P, total P, and $SO_4^{-2}$. At the end of each time series, the set of soil columns were sliced into 2-4 cm increments, and water extractable and bicarbonate extractable phosphorus (Olsen-P) was determined to examine downward phosphorus movement. Results of the study showed that Olsen-P levels were not affected

by the gypsum treatment, indicating no interference of gypsum treatment with the P-supplying capacity of soils. The gypsum treatment reduced water-extractable P levels in the high-P soil, but treatment effect was not significant in the low-P soil. Likewise, in the high-P soil, gypsum treatment resulted in leachate ortho-P reduction during the second and third period of collection. For the low-P soil, there was no significant reduction in ortho-P. Overall, these results indicated that the beneficial effect of gypsum on phosphorus export from agricultural fields is dependent on soil-P status and time interval between gypsum amendment and P fertilizer application.

Dr. Pierre-Andre Jacinthe, PhD, Chair

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

# I. INTRODUCTION

## 1.1. Statement of Problem

Phosphorus (P) is a critical plant nutrient but also a primary factor in eutrophication and impairment of surface waters. Nutrient enrichment of fresh waters causes an increase in biological productivity and leads to algal blooms and eutrophication. Excess phosphorus in streams and rivers most often originates from manure and inorganic fertilizers applied to agricultural fields (Watts and Torbert, 2009). In a large portion of the US Midwest, soils are poorly drained, and the installation of subsurface tile drains is necessary to remove excess moisture from the fields and allow farming operations to take place. This hydrological alteration greatly enhances the transport of biologically-available phosphorus to nearby creeks/streams, thus increasing the threat to aquatic ecosystems health. Several studies (Brauer, *et al.,* 2005; Bryant, *et al.,* 2012; Favaretto, *et al.,* 2012; Stout, *et al.,* 2003; and Watts and Torbet, 2009) have documented the benefits of gypsum ($CaSO_4 \cdot H_2O$) for the purposes of reducing phosphorous loss in leaching and runoff from agricultural fields. Leachate has generally been less concerning in regard to phosphorus export due to the reactivity of phosphorus in soil. However, with the use of artificial drainage systems in Indiana, phosphorus can be exported in leachate more easily (Favaretto, *et al.* 2012). It has generally been assumed that added calcium, as gypsum, aids in the reduction of dissolved reactive phosphorus (DRP) or ortho-P in leachate and agricultural runoff through adsorption and precipitation of phosphorus as calcium-phosphate minerals (Brauer, *et al.,* 2005; Bryant, *et al.,* 2012; Favaretto, *et al.,* 2012; Stout, *et al.,* 2003; and Watts and Torbet, 2009). The effectiveness of gypsum application may be dependent on the timing of fertilizer

application relative to gypsum application and the soil type to which gypsum is applied. Therefore, timing of gypsum application must be tailored in order to also maintain the phosphorus-supplying capacity of soils.

## 1.2. Consequences of Excess Phosphorus

Phosphorus is a major contributing factor to the impairment of surface water bodies in the United States (Sharpley, *et al.,* 2003). The most common type of freshwater impairment is eutrophication, nutrient enrichment of aquatic systems, and often leads to harmful algal blooms. Eutrophication occurs when there is a large in-flux of nutrients. The increase in nutrient availability causes an increase in primary productivity, and ultimately a decrease in dissolved oxygen and biodiversity (Correll, 1998). Eutrophication is natural in the aging of lakes and streams as nutrients accumulate; however, anthropogenic activities have accelerated this nutrient enrichment process (Sharpley, *et al.*, 2003).

Public awareness of the occurrence of eutrophication has grown in recent years due to its impact on surrounding communities. Water usage for recreational activities such as fishing, swimming, and as a source of drinking water are negatively impacted by eutrophication (Sharpley, *et al.*, 2002). These periods of water quality impairment have been reported in communities across different geographical regions of the United States. For example, the Eagle Creek Reservoir, a primary source of drinking water to the Indianapolis Metropolitan area, has experienced seasonal eutrophic events during summer months, leading to blooms of blue-green algae, or cyanobacteria resulting in taste and odor problems in drinking water distributed to the population (Song, *et al.*,

2013). In 2011, the western Lake Erie Basin experienced a large eutrophication event 4 times larger than the average size of such events in the previous decade. The 2011 event was linked to a large influx of bioavailable phosphorus from surrounding agricultural lands combined with a very wet spring (Michalak, *et al.*, 2013). In addition to these local events, the export of nutrients from agricultural fields in the Midwest has also been associated with the formation of the zone of hypoxia in the Mississippi River Delta, also known as the "dead zone" in the Gulf of Mexico. In 2015, the zone of hypoxia in the Gulf of Mexico was larger than the five-year average, covering an area of 16,775 $km^2$. The Gulf "dead zone" is the second largest, human-derived hypoxic area in the world (NOAA, 2015).

### 1.3. Best Management Practices for Reducing Phosphorus in Runoff

Phosphorus is a major plant nutrient, often the limiting element of ecosystem productivity. In agricultural systems, applications of manure and phosphorus fertilizers are periodically made to maintain soil fertility (Correll, 1998). A study conducted in Australia (McLaughlin *et al.*, 2001) found that more phosphorus is applied to soils (300-500 kt P/yr) than what is removed in agricultural products (120 kt P/yr in plant and animal products). Therefore, there is a significant amount of phosphorus that remains in the soils and available for removal via runoff or leaching (Favaretto, *et al.*, 2006; McLaughlin *et al.*, 2001). Since only a small fraction of the phosphorus applied is taken up by crops, a surplus of phosphorus often develops in agricultural soils. Although other factors, such as soil type and climate, can play a role, in general the higher the phosphorus content, the higher the risk of phosphorus enrichment in nearby water

systems. In addition to its negative environmental impact, phosphorus export from agricultural fields also represents a monetary loss for the farmers who may end up spending more than necessary on fertilizers (Sharpley, *et al.,* 2004*)*.

Through adoption of various regulations, progress has been made in reducing phosphorus discharge from point sources, such as water treatment facilities and industrial sites. However, this regulatory approach is difficult to apply to non-point sources of pollution, such as agricultural runoff. To address eutrophication and water quality impairment problems in agricultural areas, best management practices (BMP) must be implemented at the field level. Widespread participation of farmers is needed to make a significant difference in affected areas. It is important to manage the sources of phosphorus as well as the transport of phosphorus from fields. A common practice to reduce phosphorus in runoff includes using minimum tillage or no till or the use of vegetated buffers. However, these types of best management practice (BMP) are only known to reduce particulate phosphorus losses via surface runoff. Several studies have reported a limited effect of no till on the export of ortho-P in leachate through subsurface tile drain systems (Dayanto *et al*., 2017; Michalak *et al*., 2013) or using grass/vegetated buffers (Watts and Torbert, 2009).

### 1.4. Mechanisms for Reducing Phosphorus Solubility

Application of gypsum on agricultural soils or onto buffer strips has been shown to reduce phosphorous leaching, especially in areas where it is common practice to use manure as a source of phosphorus. Manure application may lead to soil phosphorus accumulation, creating an increased potential risk of eutrophication of surface waters. In

soils where excess phosphorus has accumulated, gypsum can benefit the surrounding ecosystems by reducing the transport of phosphorus from agricultural fields. BMP's such as no-till can help control phosphorus export through reduction in the amount of sediment material and particulates displaced during runoff events (Dayanto *et al.*, 2017; Brauer, *et al.,* 2005). Unfortunately, sediment runoff reduction only affects phosphorus in the solid phase (Bennett, *et al.,* 2001). Phosphorus in solution can be protected from leaching loss through precipitation and adsorption of phosphate ions onto mineral surfaces (McLaughlin, *et al.,* 2011). Several studies have reported significant reduction in phosphorus loss as ortho-P and as sediment-bound phosphorus through application of gypsum to agricultural fields. The positive effect of gypsum on phosphorus export has also been demonstrated in buffer strips (Bryant, *et al.,* 2012) and agricultural drainage ditches (Watts and Torbert, 2009).

The application of gypsum provides excess calcium to immobilize dissolved phosphorus; addition of $Ca^{2+}$ as an electrolyte reacts with phosphorus and allows for mitigation of excess phosphorus in leachate (Favaretto, *et al*., 2012). The most common mineral thought to be formed as a result of this reaction is DCPD, or dicalcium phosphate dihydrate, $CaHPO_4*2H_2O$ (McLaughlin, *et al.,* 2011*)*. DCPD is soluble enough to allow for continued availability of phosphorus for plant uptake. Over time, $Ca\text{-}PO_4$ complexes eventually evolve into less soluble minerals such as hydroxyapatite and fluorapatite (Watts and Torbet, 2009). As phosphorous is transformed into less soluble minerals, phosphorus leaching loss is expected to be further minimized (Favaretto *et al*., 2012). Hydroxyapatite and fluorapatite take the longest amount of time to develop in soils. When a source of phosphorus is applied, such as monoammonium phosphate (MAP),

dicalcium phosphates form. Then octacalcium phosphates begin to develop around the DCPD. According to Jones and Jacobsen (2002), octacalcium phosphate is much more soluble than the next mineral in the series, TCP or tricalcium phosphate ($Ca_3(PO_4)_2$). If TCP is the major Ca-P bearing mineral present in the soil, soluble phosphorus levels are likely to be too low for plant uptake (Jones and Jacobsen, 2002). Eventually, apatite minerals will begin to form. The initial minerals formed, such as DCPD, are more soluble and can equilibrate with the soil solution. As the mineral becomes more insoluble, equilibrium with soil solution is more difficult to achieve.

Many studies have evaluated the ability of gypsum to reduce phosphorus exported from agricultural fields, but little information exists on when gypsum should be applied in relation to crops planting and application of phosphorus fertilizer. Gypsum application rate and timing depend on the intended purpose of the gypsum. According to Chen and Dick (2011), gypsum applied to land as a sulfur fertilizer may be applied at a normal rate of 0.34 Mg $ha^{-1}$ before planting, either surface-broadcast or incorporated. A different study cited in Chen and Dick (2011) suggested that, in order to improve water quality, gypsum should be surface-applied at a normal rate of 6.73 Mg $ha^{-1}$, and may be applied 1-180 days prior to planting. This is a wide range of time in which reactions may occur in gypsum-treated soils. Too early of a gypsum application may not be effective at reducing phosphorus transport to the surrounding environment, but if gypsum is applied only 1 day prior to planting (and phosphorus fertilizer is applied at the same), rapid reactions with Ca and P may decrease the availability of phosphorus to seedlings. These recommendations are rather vague and cited studies do not emphasize the reasoning

behind the suggested time of application. Therefore, the application time relationship between gypsum and phosphorus fertilizer deserves further investigation.

## 1.5. Background

### *1.5.1 FGD gypsum*

Since the implementation of the EPA's Clean Air Act Amendment of 1990, coal-burning power plants are required to reduce nitrogen-oxides and sulfur-oxides in gas emitted. Flue-gas desulfurization (FGD) gypsum has been produced as a byproduct of that process. FGD gypsum is formed when flue gas steam passes through limestone-forced oxidation scrubbers. In the scrubbers, powdered limestone mixed with water is sprayed into the flue gas to capture sulfur (US DOE, 2013). $SO_2$ reacts with $CaCO_3$, forming calcium-sulfite which, with further oxidation, produces $CaSO_4$, or gypsum. The product can be additionally washed to remove harmful constituents, such as boron and mercury. This process removes $SO_2$ from the coal power plant's flue gas production. The gypsum produced is high quality and suitable to be used in drywall and agriculture (Chen and Dick, 2011). In 2012, more than 23 million Mg of gypsum was produced in power plants around the United States. This number is expected to increase with more power plants implementing scrubbing processes to comply with recent EPA regulations (Watts and Dick, 2014).

Gypsum has been used to improve soils in the United States since the 18$^{th}$ century (Fisher, 2011). The benefits of gypsum addition to soils are well known and include fertilizing and conditioning soil (Chen and Dick, 2011). Natural gypsum has been used as a fertilizer around the world for hundreds of years. With a massive increase in production

of synthetic gypsum, or FGD gypsum, a better understanding of how it can be used most efficiently to improve soil quality and decrease agriculture's impact on the environment should be evaluated.

Gypsum has been known to benefit soils in numerous ways. The most direct benefit of applying gypsum to agricultural fields is the addition of high concentrations of calcium and sulfur. These are essential nutrients for plant growth and certain plants require much more than what may be naturally available in soils. Gypsum can also help manage acidic soils, or soils with a pH less than 5. Sulfur is an essential nutrient for plant growth, necessary in the synthesis of amino acids and proteins essential for plant growth (Fisher, 2011). The addition of gypsum to soil as a fertilizer has proven to be effective for many crops, including corn and soybeans. Prior to 1990, studies have shown no benefits of gypsum as a fertilizer because atmospheric S deposition at that time was sufficient to meet crop S requirements. With the decrease in atmospheric sulfur deposition, it is important to consider widespread use of gypsum to maintain soil S levels (Chen and Dick, 2011). A study in Wooster, Ohio showed a drop in sulfur deposition from 1971 to 2001. In 1971, 13.6 kg $ha^{-1}$ of sulfur was deposited, and in 2001, 7.7 kg $ha^{-1}$ of sulfur was deposited from the atmosphere (Fisher, 2011). Calcium is an important nutrient for many root crops, such as peanuts. Calcium travels through plants very slowly, if at all; so, it is important that calcium is available for root uptake (Chen and Dick, 2011). Calcium is necessary to produce disease free peanuts, melons, and tomatoes (Baligar, *et al.*, 2011). Calcium also aids with building cell walls and plant structures, as well as root development, and growing fruits (Fisher, 2011).

A special characteristic of gypsum is that it is 200 times more soluble than lime, or $CaCO_3$, which is also commonly used as a soil amendment. When applied to soil surface, gypsum is more likely to dissolve and infiltrate deeper into the soil profile. Physical characteristics of soils can be improved with gypsum as a soil conditioner. Added calcium reduces dispersion of soil particles and improve aggregation of soil particles. Improved soil aggregation increases infiltration and reduces surface crusting and compaction, allowing plants to penetrate deeper into the soil. As a result, plants are more likely to withstand drought conditions (Baligar, *et al*., 2011).

### *1.5.2. Phosphorus Cycling*

An understanding of the phosphorus cycle is a first step toward proper management of soil phosphorus and protecting water quality. Phosphorus is an extremely reactive element in natural systems. Phosphorus cycling in natural environments requires knowledge of the inorganic and organic forms of phosphorus present, the biological availability of these phosphorus pools, and exchange of phosphorus between solid phases and the soil solution. For agriculture, the purpose of understanding phosphorus cycling is to ensure that enough plant available phosphorus is present for adequate crop growth. The environmental concern of phosphorus cycling is to ensure that phosphorus applied is not excessive and does not endanger nearby freshwater ecosystems. Soil P cycling must be understood, as well as managed, to achieve appropriate plant available phosphorus without posing a threat to the environment (Pierzynski, *et al.,* 2005).

There are multiple processes effecting phosphorus cycling in soil because there are also many forms of phosphorus present. Phosphorus used by plants exists as

phosphate, $HPO_4^{-2}$ or $H_2PO_4$, depending on soil pH. Phosphorus also exists as organic P, as P sorbed to minerals, and in P-bearing minerals. The processes controlling how much plant available phosphorus is present at a given time include: mineralization and immobilization by soil microbes, sorption and desorption, dissolution-precipitation of phosphorus bearing minerals, and oxidation and reduction reactions. Sorption occurs when there is a large presence of positively charged ions in soil minerals. Iron and aluminum are commonly found in minerals to which phosphate will be chemically attracted to. This is more likely to occur in soils with a lower pH due to a greater presence of positively charged particles and in finer textured soils because of a greater amount of surface area. Sorption of phosphorus decreases when there are other negatively charged ions, such as carbonate or bicarbonate, present to compete for sorption sites (Jones and Jacobsen, 2005). Mineralization of phosphorus occurs when organic phosphorus is decomposed and is converted to phosphate, or plant available phosphorus. This occurs more readily when the C:P ratio is less than 200:1. Immobilization occurs when phosphorus becomes tied up in soil microbial biomass and thus no longer available for plant uptake. This is most likely to happen when C:P ratio is greater than 300:1. The balance between net P immobilization versus net P mineralization is also influenced by temperature, aeration, and pH due to the effect of these factors on microbial activity (Jones and Jacobsen, 2005).

## 1.6 Project Significance

Research regarding phosphorus in soil and its reactions with gypsum should be further explored to gain a better understanding of how phosphorus behaves in gypsum-

treated agricultural fields. The literature is clear in that in soils containing excessive amounts of available phosphorus, gypsum application can benefit the environment through reduction of the amount of phosphorus transported via leaching. However, there is a lack of information in the literature as to how the timing of gypsum application could affect soil phosphorus leachability and its downward migration in the soil profile.

The phosphorus holding capacity of gypsum-treated soils needs to be better understood to determine both the water quality improvement benefits and the phosphorus deficiency risks associated with gypsum application to agricultural soils. An improved understanding of gypsum amendment as an agricultural practice would allow for better use of resources and provide economic benefit to farmers and land managers. The overarching goal of this research is to develop quantitative information regarding gypsum application with respect to timing of fertilizer application to achieve intended benefits, specifically regarding the dynamics of soil phosphorus.

## 1.7. Research Objectives

-Investigate the effects of the time interval between gypsum treatment and phosphorus fertilizer applications on the effectiveness of gypsum in reducing phosphorus leaching in soils with contrasting levels of total P.

- Investigate Ca-P interactions and their effect on the availability of phosphorus and its downward mobility in gypsum-treated soil columns.

## II. MATERIALS AND METHODS

### 2.1. Soil sampling and characterization

Soils used in these experiments were selected to represent fields with contrasting soil P status: a low-P soil and a high-P soil. It is known from the literature that soils with high phosphorus levels are more likely to experience greater phosphorus loss via subsurface pathways than low-P soils (Favaretto, *et al.,* 2006). The high-P soil is a Fincastle silt-loam (fine silty mesic Aeric Epiaqualf), and was collected from a cropped field managed by Legan Livestock and Grain, Inc. near Coatesville, IN (39° 37’ 54” N, 86° 42’ 57” W). The Legan family raises hogs and utilizes hog manure as a fertilizer for crops. Soils in that field have registered high phosphorus levels since Mark Legan purchased the farm in 1989. The low-P soil was collected from Starkey Farms near Brownsburg, IN (39° 53' 38" N, 86° 21' 4" W). At that location, the dominant soil series include Brookston (fine-loamy, mesic Typic Argiaquoll) and Crosby (fine, mesic Aeric Epiaqualfs). At both locations, soils are developed from Wisconsinan glacial till underlain by dolomite and limestone bedrock.

After collection (0-30 cm depth), soils were thoroughly mixed, clumps were broken up, homogenized by passing through a 3.4 mm sieve, and stored in large plastic containers in a greenhouse. Soil was periodically moistened and kept moist until the start of the experiment described below. Composited soil sub-samples from each site were analyzed for background properties including organic carbon, total P and available P.

2.2. Packing of soil columns and amendment with gypsum

The experiment was conducted in a greenhouse located atop of the LD building on the IUPUI campus. The experimental design included: 2 soil types (low P, high P), 2 gypsum application rates (0 Mg $ha^{-1}$and 5.0 Mg $ha^{-1}$) and 3 P-fertilizer application times (2 days, 4 weeks, and 8 weeks post gypsum application). Each treatment was run in triplicate, for a total of 36 experimental units. Leaching experiments were conducted using soil-filled PVC columns (10- cm diameter and 20-cm long). Before packing the columns, the bottom of the PVC pipe was fitted with a piece of fiberglass screen attached to the PVC wall using caulk. A layer (3 cm) of acid-washed pea gravel was placed on top of the fiberglass screen. The bottom of each column was closed with a PVC cap, tightly caulked to the PVC pipe wall and fitted with a 1.2 cm hole drilled at its center for drainage. Finally, a plastic spout was securely affixed to the drainage hole to channel leachate into a sampling container.

Each column was filled with 1.4 kg of sieved soil (3.4 mm) to achieve a density of 1.2 g $cm^{-3}$. Soil was packed in 4 cm increments to achieve appropriate bulk density. Packed columns were water-saturated through capillary action (from the bottom), then drained overnight. In the greenhouse, columns were placed on 10.2-cm tall wooden blocks to create enough clearance to fit sampling bottles below the columns. Within 24 h of soil packing, half of the columns (18) were treated with gypsum and the other half remained untreated (controls).

Gypsum (2.78 g $kg^{-1}$ soil or 3.9 g per column) was applied evenly at the surface of each gypsum-receiving column and mixed in the top 2 cm soil layer. This is equivalent to a field rate of 5 Mg $ha^{-1}$. This rate was selected based on past experiments that have this

level of gypsum addition to be effective in reducing the leaching of soluble phosphorus in agricultural soils (Brauer, *et al.,* 2005; Watts and Torbert, 2009).

2.3. Phosphorus fertilizer application and leachate collection

As stated earlier, one of the objectives of this study was to determine whether the time gap between gypsum amendment and phosphorus fertilizer application affects gypsum-treatment efficiency. In this study, we investigated 3 different time intervals between these two operations: short (2 days), medium (28 days) and long (56 days) intervals. Consequently, the columns were divided into 3 sets (each set: 3 treated and 3 controls) to accommodate each of these time gaps. At the appropriate time interval (ie. 2, 28- or 56-days following gypsum amendment), phosphorus fertilizer application was made in the form of a solution of $KH_2PO_4$ and at an equivalent field rate of 34 kg P $ha^{-1}$ (Kost, *et al.* 2014). To induce vertical phosphorus movement, soil columns were periodically watered with rainwater in amounts reflecting local conditions. Analysis of Central Indiana rainfall data (1991-2014) has shown that, during the dormant season (October – March), the region receives on average 473 mm of rainfall in about 64 events, or approximately 7.4 mm per event. This is equivalent to 58 mL of rainwater per soil column (surface area: 78 $cm^2$) for each simulated rainfall event. For this experiment, rainfall was collected in an open area on February 2, 2016 and was used to simulate rainfall input. Rainwater was stored in a refrigerator at $4^o$ C for the duration of the experiment. Analysis of rainwater sub-samples were conducted (pH: 7.23; EC: 0.12 dS $m^{-1}$; SRP: <9 μg $L^{-1}$; TP: 244.6 μg $L^{-1}$; $SO_4^{-2}$: 8.52 mg S $L^{-1}$).

Following phosphorus fertilizer application to the soil columns, leachate was collected every two days for the first week, and then every four days for a total of 28 days. Leachate was collected in acid-washed high-density polyethylene bottles and transferred to 50 ml polypropylene centrifuge tubes to be stored in a freezer until analysis. Leachate volume was also recorded.

## 2.4. Phosphorus distribution in soil columns at the end of the experiment

Upon completion of each set of leaching experiments, the soil columns were sliced in 2-4 cm segments to determine the variation with depth of phosphorus and assess its downward mobility in gypsum-treated soil columns. The depth distribution of phosphorus could therefore provide another way to determine whether gypsum application could effectively control downward migration of phosphorus in agricultural soils. Soil samples were air-dried, sieved (2 mm) and extracted for Olsen-P and water-extractable P. Olsen-P is a soil extraction procedure using a bicarbonate solution to represent the pool of plant available phosphorus.

## 2.5. Analytical procedures

### *2.5.1. Soil analysis*

Prior to the experiment, initial soil pH was measured potentiometrically in a suspension (1:2 soil:water ratio) with a pH meter (Accumet model 25 pH/ion meter). Organic carbon was measured by dry combustion at 960 °C on a Vario-Cube C-N analyzer (Elementar Americas, NJ) using finely-ground (150 µm) soil sample aliquots weighted (6-8 mg) in tin capsules. Soil organic matter was measured by the loss on

ignition (LOI) method as the net mass loss following combustion (450 °C, 3 h) of soil sub-samples (2 g) in a furnace. Ash from the LOI test was used for determination of total P (Anderson, 1976). Briefly, 0.2 g of ash material was placed in glass Pyrex tubes and treated with 20 mL of 1 N HCl. The suspension was placed in a boiling water bath for 15 min, centrifuged (3,000 rpm for 5 min), and filtered using Whatman 42 filters. A filtrate aliquot (10 ml) was diluted with deionized water to achieve a total volume of 50 ml. The concentration of phosphorus in the diluted filtrate was determined using molybdate colorimetry (EPA method 365.3), and total P was computed.

The amount of available P was assessed by water extraction and by the Olsen method (extraction with 0.5 M sodium bicarbonate, $NaHCO_3$). Water extractable P was measured by combining 1 g of soil with 20 mL of milli-Q water in a centrifuge tube. The suspension was shaken for 30 min and centrifuged for 5 min at 3,000 rpm,a nd then filtered (Whatman 42). The filtrate was analyzed for SRP concentration using EPA method 365.3.

For the Olsen method, duplicate (1 g) soil samples were placed in centrifuge tubes and treated with 20 mL of 0.5 M sodium bicarbonate extracting solution. A small scoop of activated charcoal was added to minimize background color. The suspension was shaken for 30 min and centrifuged for 5 min at 3,000 rpm. The supernatant was filtered (Whatman 42) and the filtrate was analyzed for SRP.

*2.5.2. Chemical analysis of leachate*

Soil column leachate was analyzed for electrical conductivity (EC), pH, $SO_4^{-2}$, soluble reactive P, and total P. Electrical conductivity, a measure of dissolved solids in

solution, was measured using a conductivity-meter (Acumet model 25 pH/ion meter). Soil and leachate pH was measured using a calibrated Acumet pH meter.

The concentration of soluble reactive P (SRP) was measured using EPA method 365.3 on an Aquachem Konelab analyzer (samples from days 2-40) and EPA method 145-A on an AQ400 (Seal Analytical, Mequon, WI) analyzed (samples from days 44-80). On both analyzers, SRP detection is based on the formation of a blue phosphor-molybdate complex in an acidic medium in the presence of ammonium tartrate and ascorbic acid.

To determine dissolved total P, leachate subsamples were digested using acid persulfate (130.4 g $L^{-1}$) and autoclaving (120 °C, 15-20 psi, 30 min) as described by Williams *et al* (1995). The concentration of SRP in the digested sample was determined by the molybdate colorimetric method described above, With each batch of samples, phytic acid solutions of known phosphorus concentrations were also autoclaved and analyzed to assess percent phosphorus recovery of the autoclaving method (Williams *et al*., 1995).

The concentration of $SO_4^{2-}$ in leachate was monitored to determine the extent of the gypsum leaching out of the soil columns. Due to limited leachate volume collected on some sampling dates, data on $SO_4^{2-}$ was incomplete. Leachate sub-samples were analyzed for $SO_4^{2-}$ on selected dates using a turbidimetric procedure (EPA method 165-A) on an AQ400 analyzer.

## 2.6. Statistical Analysis

Data were analyzed using two-way analysis of variance (ANOVA) to assess the effect of experimental factors on column leachate volume and composition (pH, EC, ortho-P, organic P, $SO_4^{2-}$). For this analysis, the class variables were initial soil P level (low or high P), gypsum application rate (0 or 5 Mg $ha^{-1}$), and timing of fertilizer application (2 days, 28 days, or 56 days after gypsum). The analysis was conducted using the repeated measures two-way ANOVA in PAST 4.0 with sampling date as the repeated measure factor. When a significant treatment effect was detected, separation of treatment means was done using t-test. Unless otherwise noted, statistical significance was determined at $P < 0.05$.

## III. RESULTS

### 3.1. Chemical characteristics of soils used in the experiment

The two soils selected for this study were circum-neutral with pH ranging between 6.9 and 7.3 (Table 1). As expected, the soil collected from the manure-treated field obtained from the manure treated field had significantly ($p<0.005$) higher levels of total P levels than the soil taken from the conventionally fertilized field. Soil organic matter and organic carbon concentration was also much higher in the manure-treated soil. Total nitrogen concentration was similar, but the C/N ratio of soil organic matter was higher (13.8) in the high-P soil than in the low-P soil (10).

Table 1. Soil chemical properties. Within a column, values followed by different letters are significantly different ($P<0.05$)

| Soil type | Soil pH | Total P mg P $kg^{-1}$ soil | Organic matter, % OM | Organic carbon, % C | Total nitrogen, % N |
|---|---|---|---|---|---|
| Low-P | $7.05_a$ | $460.8_a$ | $0.77_a$ | $1.4_a$ | $0.14_a$ |
| High-P | $7.19_a$ | $4636.4_b$ | $1.37_b$ | $1.8_a$ | $0.13_a$ |

### 3.2. Leachate Volume

Results of the two-way ANOVA test (Table 2) showed that, for either soil type, the gypsum treatment alone did not have a significant ($P<0.05$) effect on the volume of leachate produced. However, the timing of phosphorus application relative to gypsum treatment had a significant effect on the amount of leachate produced, irrespective of soil type. In the low-P soil, there was a significant ($P<0.05$) interaction between gypsum treatment and timing of fertilizer application.

Table 2. ANOVA results for the effect of gypsum treatment and timing of phosphorus fertilizer application of the volume of leachate collected from the soil columns. Results are presented each soil type (high-P and low-P) separately. * indicates P<0.05, ** indicates P<0.01, and ns indicates not significant.

| Class variables | df | Low- P soil | High-P soil |
|---|---|---|---|
| Gypsum | 1 | ns | ns |
| Timing | 2 | ** | ** |
| Gypsum X Timing | 2 | * | ns |

Table 3. Average volume of leachate (mL) collected from untreated and gypsum-treated soil columns at different time periods during the experiment. Results are presented separately for each soil type (low-P, high-P) Data are mean ± standard deviation of 24 measurements. Within a column and for a given soil type, values followed by different letters are significantly different.

| Time period, days | Untreated | Gypsum-treated | Untreated | Gypsum-treated |
|---|---|---|---|---|
| | Low-P soils | | High-P soils | |
| 2-24 | $40.4_a \pm 15.3$ | $30.9_a \pm 18.8$ | $38.2_a \pm 19.2$ | $33.0_a \pm 20.1$ |
| 30-52 | $41.0_a \pm 8.1$ | $44.4_a \pm 8.6$ | $49.5_a \pm 6.2$ | $47.7_a \pm 8.9$ |
| 58-80 | $49.6_a \pm 7.3$ | $51.5_a \pm 8.6$ | $50.8_a \pm 12.0$ | $54.2_a \pm 4.9$ |

During the first collection period (2-24 days after gypsum application) of the experiment, the gypsum-treated columns produced a lower amount of leachate than the untreated columns. Although the gypsum treatment was not always significant, the overall trend of lower leachate volume in gypsum-treated columns consistently observed through that period (Fig. 1). For the low-P soil, the volume of leachate from the gypsum-treated columns was significantly (P<0.05) less than in the untreated columns between 8 and 12 days after gypsum application (Fig. 1) Likewise, for the high-P soil, the gypsum-treated columns at 8 and 16 days after gypsum application (Fig. 1).

During the second period (30-52 days after gypsum application) and third period (58-80 days after gypsum application) of the experiment, there was no clear effect of the gypsum-treatment on leachate volume (Figs. 2-3). Instances of both higher and lower leachate volume in the gypsum-treated columns than in the control columns was observed, but difference was almost always not statistically significant. Although the overall effect of soil type on leachate volume was not significant, the high-P soil columns produced more leachate than the low soil-P columns (Figs. 1-3). A decreasing trend in runoff volume was noted during the section period of the experiment (after day 40). This trend was likely due to unexpected change in temperature or humidity in the greenhouse where the experiment was conducted.

Based on the average amount of leachate produced during the first collection period (Table 3), the gypsum-treated columns produced 12.8% less leachate than the untreated for the low-P soil and 3% less for the high P soil. During the second collection period, the gypsum-treated columns produced 13.5% more leachate than the untreated for the low-P soil and 4.5% less for the high-P soil. By the third collection period, both soil types treated with gypsum produced, on average, a greater amount of leachate. Gypsum-treated columns produced 3.6% more leachate in the low-P soil and 6.9% more leachate in the high-P soil.

Figure 1. Volume of leachate during the first period of the experiment (2-24 days). ns= no significance *= P<0.05

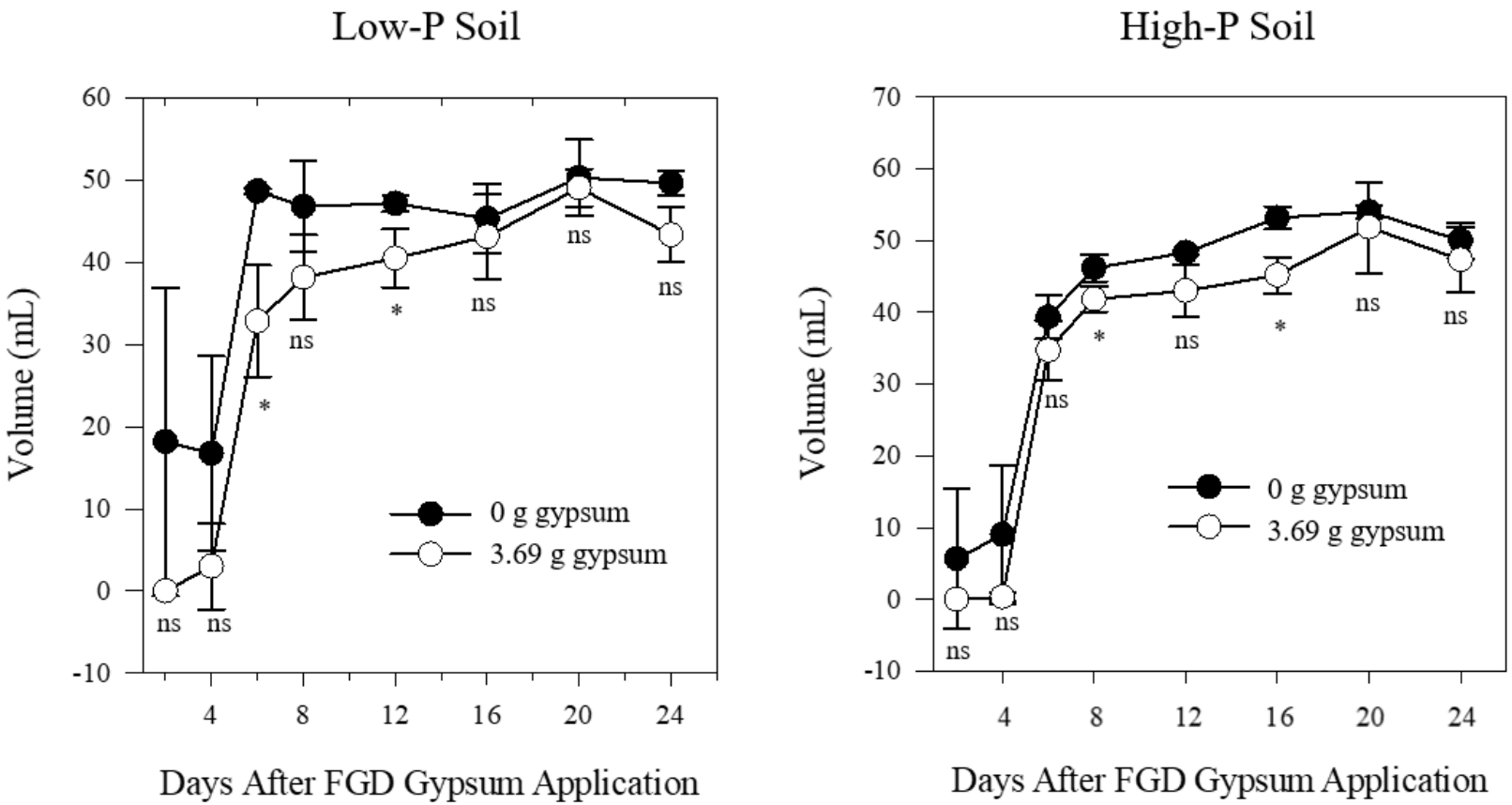


Figure 2. Volume of leachate during the second period of the experiment (30-52 days). ns= no significance *= P<0.05

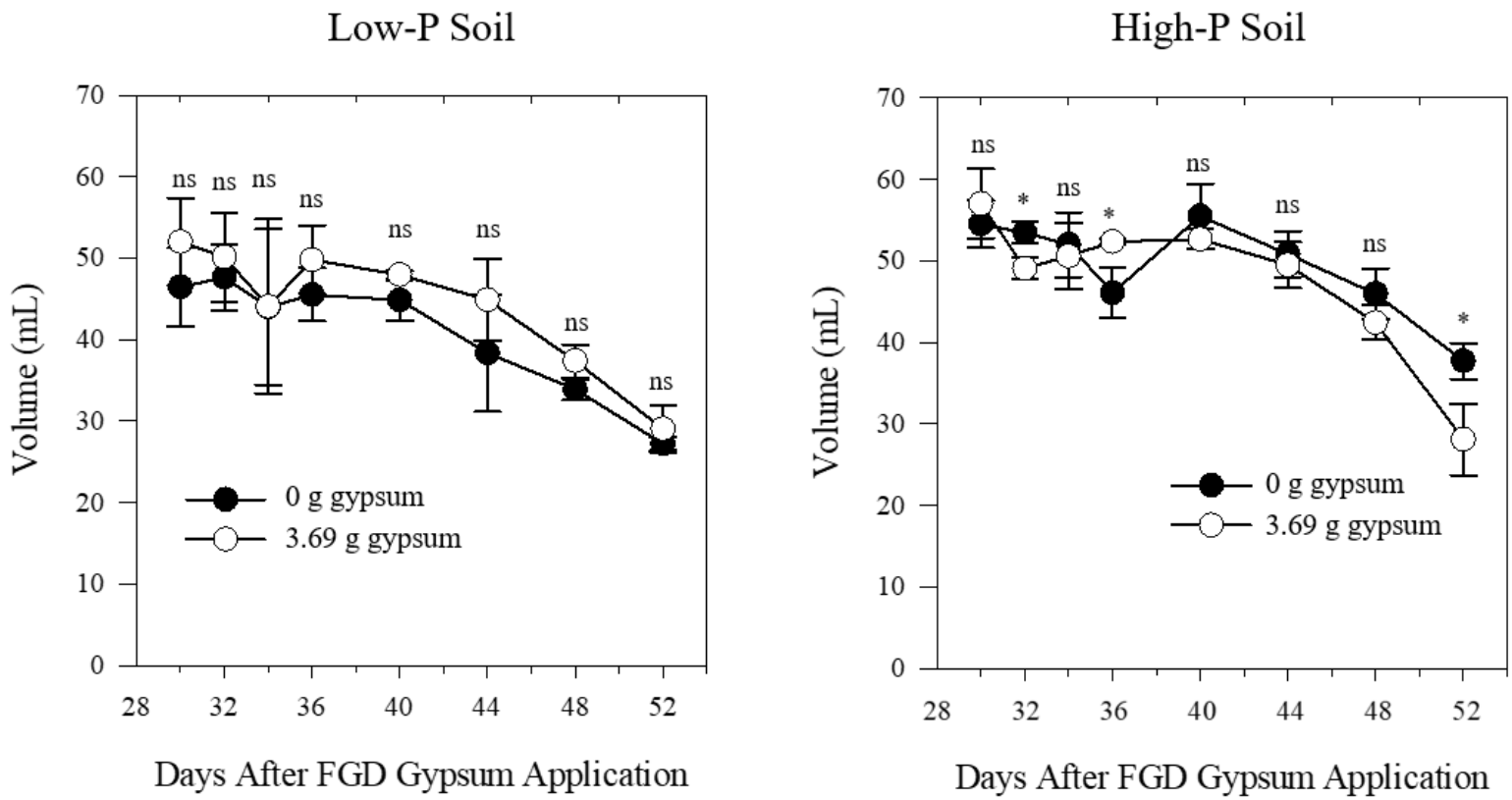
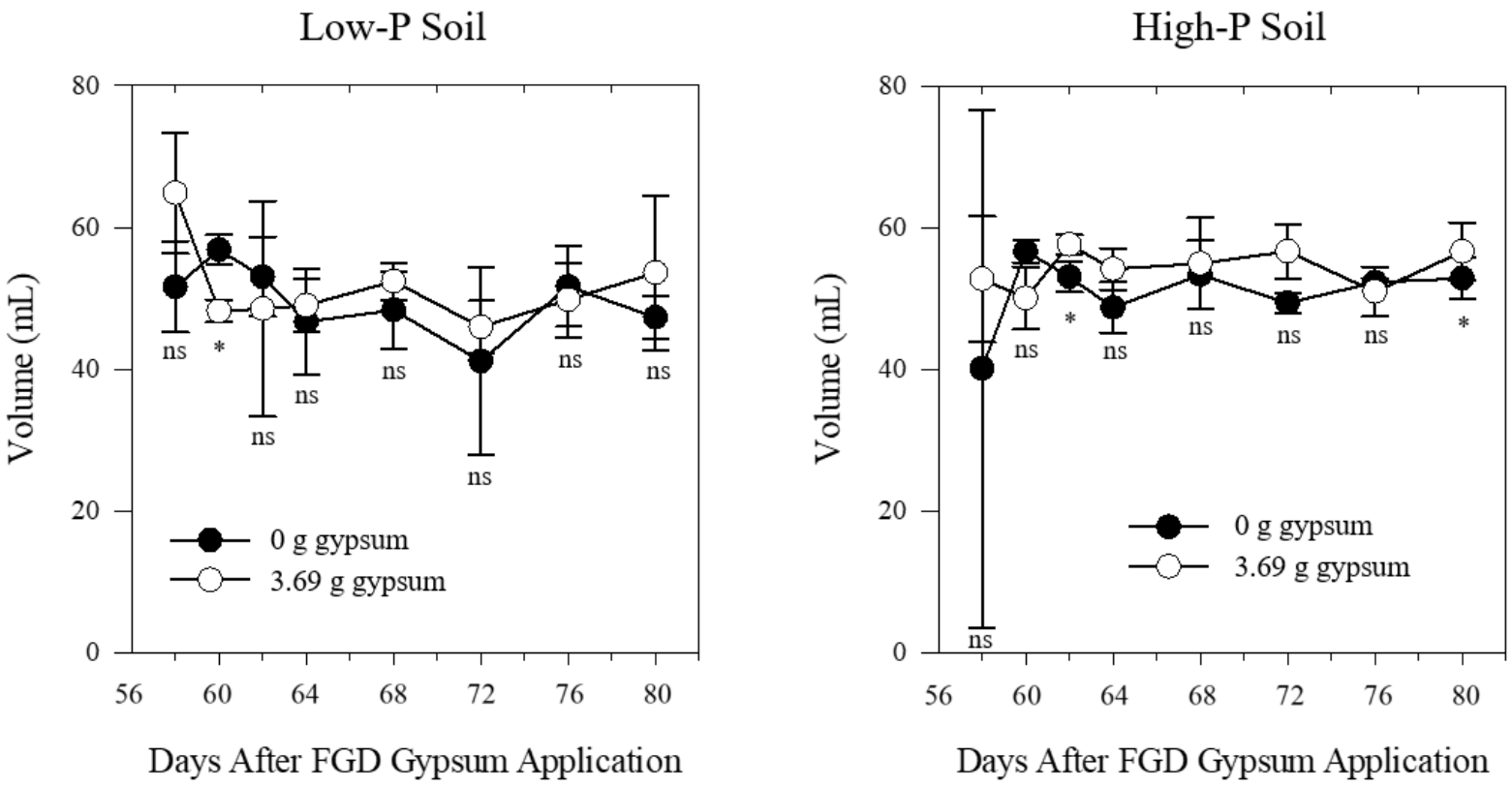


Figure 3. Volume of leachate during the third period of the experiment (58-80 days). ns= no significance *= P<0.05.



3.3. Leachate chemistry

Average pH of the leachate collected from the columns ranges between 6.7 and 8.0, with a general trend of increased pH over the duration of the experiment (Table 5) That trend was confirmed by the results of ANOVA showing a significant effect of timing of leachate pH (Table 4). There was a significant effect of the gypsum treatment between the untreated and the gypsum-treated columns during the third collection period.

Electrical conductivity (EC) of leachate ranged between 1.6 and 4.7 dS $m^{-1}$ (Table 5). During the first period of the experiment (2-24 days), EC was similar between untreated and gypsum-treated columns. However, later in the experiment (days 58-80) a significant treatment effect was detected by ANOVA (Table 4), with leachate EC from gypsum-treated columns being significantly ($P<0.05$) higher than from untreated columns. In general, leachate from the low-P soil columns had higher EC compared to leachate form the high-P soil columns.

Table 4. ANOVA results for the effect of gypsum treatment and timing of phosphorus fertilizer application on the pH and electrical conductivity of leachate collected from the soil columns. Results are presented each soil type (high-P and low-P) separately. * indicates P<0.05, ** indicates P<0.01, and ns indicates not significance.

| Class variables | df | Low-P soil | High-P soil |
|---|---|---|---|
| | | pH | |
| Gypsum | 1 | ns | * |
| Timing | 2 | ** | ** |
| Gypsum X Timing | 2 | ns | ** |
| | | Electrical conductivity | |
| Gypsum | 1 | ns | ** |
| Timing | 2 | ** | ns |
| Gypsum X Timing | 2 | ** | ns |

Table 5. Electric conductivity and pH of leachate collected from untreated and gypsum-treated soil columns at different time periods during the experiment. Results are presented separately for each soil type (low-P, high-P). Data are mean ± standard deviation of 18-24 measurements. Within a column and for a given soil type, values followed by different letters are significantly different $P<0.05$

| Time period, days | Untreated | Gypsum-treated | Untreated | Gypsum-treated |
|---|---|---|---|---|
| | Low-P soils | | High-P soils | |
| | pH | | | |
| 2-24 | 7.1a ±0.5 | 6.7a ± 1.2 | 7.2a ±0.3 | 7.0b ±0.3 |
| 30-52 | 7.4a ±0.4 | 7.5a ±0.4 | 7.5a ±0.4 | 7.5a ±0.4 |
| 58-80 | 7.7a ±.3 | 7.7a ±0.3 | 7.4a ±0.5 | 8.0b ±0.5 |
| | Electrical conductivity, dS $m^{-1}$ | | | |
| 2-24 | 2.3a ±0.6 | 2.7a ± 1.1 | 1.7a ±0.6 | 1.9a ±0.6 |
| 30-52 | 4.3a ±1.6 | 3.2b ±1.0 | 1.8a ±0.4 | 2.3b±0.5 |
| 58-80 | 3.5a ±1.5 | 4.7b ±1.6 | 1.6a ±0.5 | 2.2b ±0.7 |

3.4. Phosphorus concentration in leachate

Ortho-P concentration ranged from 12.5 to 40.6 μg P $L^{-1}$ in leachate of the low-P soil, and from 12.1 to 70.8 μg P $L^{-1}$ in leachate from the high-P soil (Table 7). ANOVA showed a highly significant ($P<0.01$) effect of timing of P fertilizer application on ortho-P concentration in leachate and a significant effect of gypsum treatment on ortho-P concentration (Table 6). Ortho-P concentration in low-P soil leachate tended to be lower (1.6-2.9 times) during the first collection period than during the second (30-52 days) and third (58-80 days) periods of the experiment (Table 7). Ortho-P concentration in leachate from the gypsum-treated, low-P soil was significantly higher during the first period (2-24 days) and was similar for the second (30-52 days) and third (58-80 days) periods. Ortho-P concentration in the leachate from the gypsum-treated, high-P soil was significantly ($P<0.05$) lower for the second (30-52 days) and third (58-80 days) periods and similar for the first (2-24 days). The gypsum-treated, high-P soil had an ortho-P reduction of 28% for the second period of collection and 45% for the third period of collection.

Average total P concentration ranged from 236.0 to 275.7 μg P $L^{-1}$ in leachate from the low-P columns, and from 249.5 to 342.7 μg P $L^{-1}$ in leachate from the high P columns (Table 7). ANOVA showed a significant effect ($P<0.01$) of timing of P fertilizer application on total P in leachate form the low-P columns, and a significant effect ($P<0.01$) of gypsum treatment on total P in leachate form the high-P columns (Table 6). For the high-P soil, total P concentration was significantly ($P<0.05$) higher in leachate from the gypsum-treated than from the untreated columns during the first collection period (2-28 days), but the opposite was observed during the second and third collection periods (1.3-fold lower concentration of total P in leachate from gypsum-treated than

from untreated columns). Total-P of the leachate collected from the gypsum-treated, high-P soil during the third period was reduced by 22%.

Table 6. ANOVA results for the effect of gypsum treatment and timing of phosphorus fertilizer application on the concentration of ortho-P and total P in leachate collected from the soil columns. Results are presented each soil type (low-P, high-P) separately. * indicates P<0.05, ** indicates P<0.01, and ns indicates no significance.

| Class variables | df | Low-P soil | High-P soil |
|---|---|---|---|
| | | Ortho-P | |
| Gypsum | 1 | * | ns |
| Timing | 2 | ** | ** |
| Gypsum x Treatment | 2 | ns | ns |
| | | Total P | |
| Gypsum | 1 | ns | ** |
| Timing | 2 | ** | ns |
| Gypsum x Treatment | 2 | ns | ns |

Table 7. Average concentration (μg $L^{-1}$) of ortho-P and total P in leachate collected from untreated and gypsum-treated soil columns at different time periods during the experiment. Results are presented separately for each soil type (low-P, high-P). Data are mean ± standard deviation of 10-24 measurements. Within a column and for a given soil type, values followed by different letters are significantly different $P<0.05$.

| Time period, days | Untreated | Gypsum-treated | Untreated | Gypsum-treated |
|---|---|---|---|---|
| | Low-P soils | | High-P soils | |
| | | Ortho-P, μg P $L^{-1}$ | | |
| 2-24 | 12.5a±9.7 | 21.0b±7.8 | 25.3a±18.6 | 29.0a±17.3 |
| 30-52 | 33.1a±20.1 | 40.6a±17.1 | 70.8a±40.4 | 50.6a±16.3 |
| 58-80 | 36.1a±13.6 | 34.3a±13.2 | 25.1a±20.1 | 12.1b ±6.0 |
| | | Total P, μg P $L^{-1}$ | | |
| 2-24 | 273.4a ±33.0 | 260.4a ±38.5 | 249.5a ±45.8 | 287.2b ±40.3 |
| 30-52 | 236.0a ±27.6 | 244.2a ±22.9 | 299.9a ±52.0 | 289.2a ±95.9 |
| 58-80 | 244.0a ±25.4 | 240.3a ±38.6 | 342.7a ±116.5 | 265.9b ±49.1 |

3.5. Sulfate concentration in leachate

For either soil type (low-P and high-P), the level of sulfate found in the leachate was significantly ($P<0.05$) higher in gypsum-treated than in untreated soil columns during the first (2-28 days) and second (30-52 days) periods. During the third collection period (58-84 days), difference in sulfate concentration between treated and untreated columns was highly significantly ($P<0.01$). For the same treatment and collection period, sulfate concentration in leachate was consistently higher in the low-P soil than in the high-P soil (Table 9).

Overall the concentration of $SO_4^{2-}$ in leachate increased progressively throughout the course of the study although, in the case of the high-P untreated soil, that trend was somewhat muted due to the lower concentration of sulfate measured in leachate from these columns (Fig. 5). In the low-P soil columns, $SO_4^{2-}$ concentration difference between untreated and gypsum-treated columns became significant at day 58 of the experiment (Fig. 4). However, in the high-P soil columns, significant differences ($P<0.05$) were noted as early as 20 days after gypsum treatment.

Table 8. ANOVA results for the effect of gypsum treatment and timing of phosphorus fertilizer application on the concentration of sulfate in leachate collected from the soil columns. Results are presented each soil type (low-P, high-P) separately. * indicates $P<0.05$, ** indicates $P<0.01$, and ns indicates no significance.

| Class variables | df | Low-P soil | High-P soil |
|---|---|---|---|
| Gypsum | 1 | ** | ** |
| Timing | 2 | ** | ** |
| Gypsum x Timing | 2 | * | ns |

Table 9. Average concentration of sulfate (mg S $L^{-1}$) in leachate collected from untreated and gypsum-treated soil columns at different time periods during the experiment. Results are presented separately for each soil type (low-P, high-P). Data are mean ± standard deviation of 6-24 measurements. Within a column and for a given soil type, values followed by different letters are significantly different $P<0.05$.

| Time period, days | Untreated | Gypsum-treated | Untreated | Gypsum-treated |
|---|---|---|---|---|
| | Low-P soils | | High-P soils | |
| 2-24 | 65.3a±30.4 | 115.2b±59.8 | 31.4a±10.5 | 84.4b±50.5 |
| 30-52 | 189.4a±84.4 | 267.5a±142.6 | 59.1a±41.7 | 202.8b±90.4 |
| 58-80 | 221.0a±75.9 | 412.9b±145.0 | 45.8a±15.6 | 277.2b±70.4 |

Figure 4. Average sulfate concentration in low-P soil leachate for each collection time. * indicates statistical significance in two-tailed T-test P<0.05.

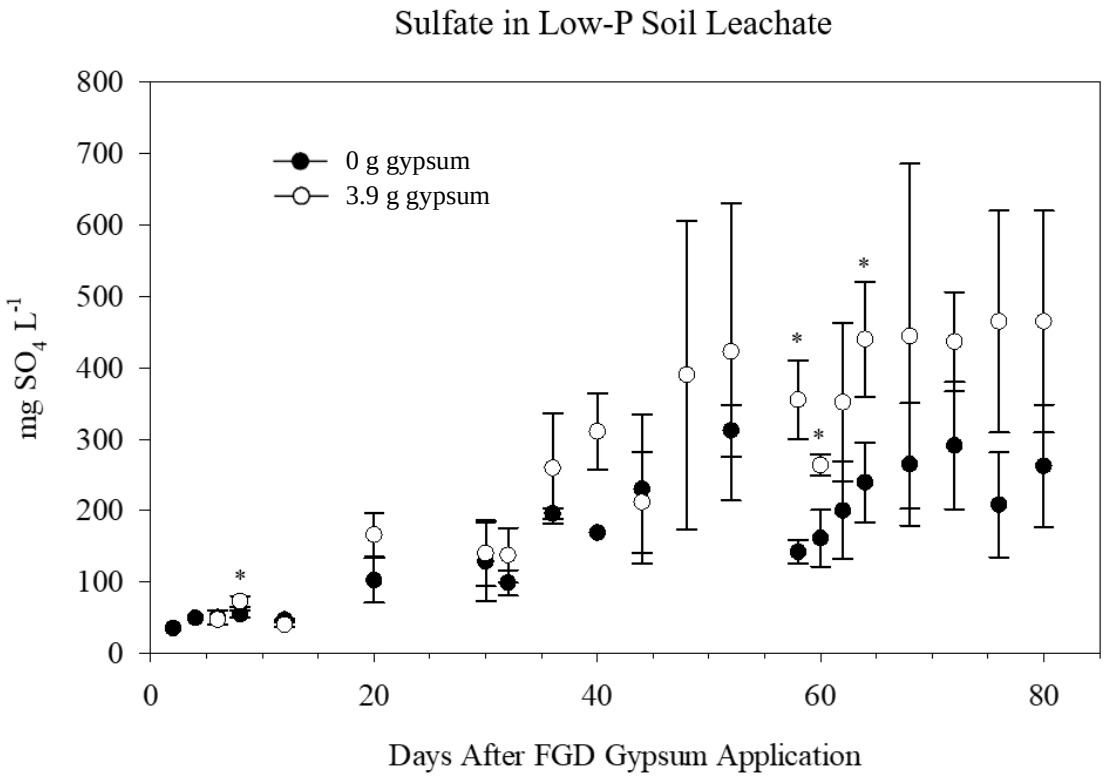
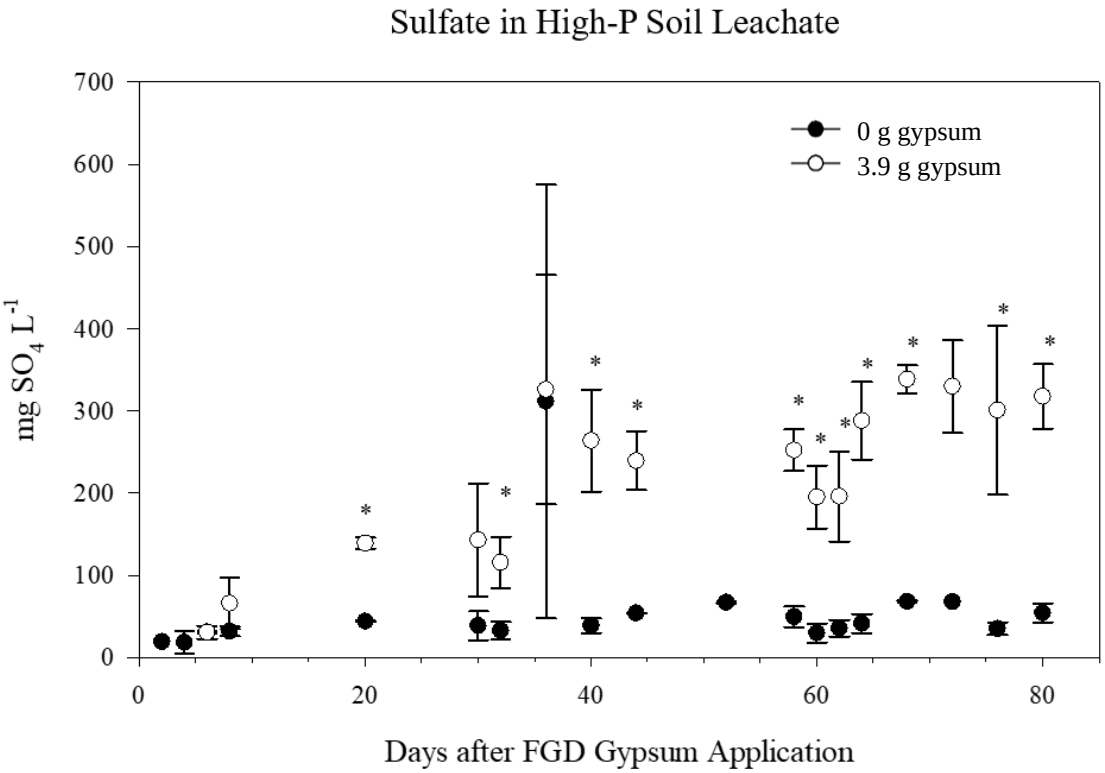


Figure 5. Average sulfate concentration in high-P soil leachate for each collection time. * indicates statistical significance in two-tailed T-test P<0.05.



3.6. Water Extractable P in gypsum-treated soils

At the end of the first 28 days of the experiment, water extractable P was lower at most soil depths (Fig. 6). In the high-P soil, although average concentration for all depths was significantly ($P<0.05$) lower in the gypsum treatment (15.7 vs 22.5 mg P kg-1 soil), difference was not statistically significant at any individual depth. In the low-P soil, water extractable P in the surfaced soil layer (0-2 cm) was significantly ($P<0.05$) lower in the gypsum-treated soil than in the control (Fig. 6).

A similar effect of gypsum amendment was observed with in the soil samples collected at the end of the second period of the experiment (56 days after gypsum amendment). In the low-P soil, water extractable P was lower in the gypsum-treated soils than in the control at every depth, and the difference was statistically significant ($P>0.05$) in the 2-4 cm and 10-15 cm layers. For the high-P soil, water extractable P concentration was also lower at every depth in the gypsum-treated soil, but difference was not significant.

At the end of the last period (84 days after gypsum amendment), water extractable P was still lower in the gypsum-treated than in the control soils at all depths for both soil types. In the low-P soil, a significant effect ($p<0.05$) of gypsum treatment was detected at the 0-2 cm, 4-6 cm, and 6-10 cm depths. In the high-P soil treated with gypsum, water extractable P was lower at every depth, but difference was only significant ($p<0.05$) at the surface layer (0-2 cm).

As expected, the average concentration of water extractable P (all depths) was several-fold (17-27 times) higher in the high-P soil than in the low-P soil. Study-wide averaged concentration of water-extractable P in the high-P soil was 22.5 and 15.7 mg P $kg^{-1}$ soil in the control and gypsum-treated soils, respectively. That corresponds to a 30%

reduction in the concentration of water-extractable P. For the low-P soil, average concentration of was 1.3 and 0.58 mg P kg-1 soil, corresponding to a 55% reduction in the pool of water-extractable P.

Table 10. Depth-averaged concentration of water-extractable P (mg P $kg^{-1}$ soil) in untreated and gypsum-treated soil columns as related to the time gap between gypsum amendment and phosphorus fertilizer application. Within a row for sampling time and for a given soil type, values followed by different letters are significantly different at $P<0.05$.

| Soil sampling, days | Time gap between gypsum and P fertilizer addition, days | Untreated | Gypsum-treated | Untreated | Gypsum-treated |
|---|---|---|---|---|---|
| | | Low-P soil | | High-P soil | |
| 28 | 2 | 1.01a ±1.18 | 0.56a ±0.24 | 20.1a ±3.52 | 15.7b ±2.98 |
| 56 | 30 | 1.06a ±2.52 | 0.57b ±0.67 | 18.6a ±2.57 | 13.0b ±2.52 |
| 84 | 54 | 1.81a ±1.15 | 0.61b ±0.19 | 26.3a ±2.22 | 18.6b ±4.26 |

Table 11. ANOVA results for the effects of gypsum treatment and timing of phosphorus fertilizer application on the water extractable P of soil collected from the columns. Results are presented by each soil type (high-P and low-P) and by each depth from which the soil was collected (0-2 cm, 2-4 cm, 4-6 cm, 6-10 cm, and 10-15 cm). * indicates P<0.05, ** indicates P<0.01, and ns indicates no significance.

| Class Variables | df | Low-P soil water extractable P | | | | | High-P soil water extractable P | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0-2 cm | 2-4 cm | 4-6 cm | 6-10 cm | 10-15 cm | 0-2 cm | 2-4 cm | 4-6 cm | 6-10 cm | 10-15 cm |
| Gypsum | 1 | ** | ns | * | ns | ns | ** | ns | * | * | ns |
| Time | 2 | ns | ns | ns | ns | ns | * | ns | ns | ns | ns |
| Gypsum X Time | 2 | ns | ns | ns | ns | ns | * | ns | ns | ns | ns |

Figure 6. Depth distribution of water extractable P in untreated and gypsum-treated soil columns at the end of the first period of the experiment. Columns were amended with FGD-gypsum at an equivalent field rate of 5 Mg $ha^{-1}$ (3.9 g per column). Phosphorus fertilizer, in the form of a solution of $KH_2PO_4$ and at an equivalent field rate of 34 kg P $ha^{-1}$, was applied 2 days after gypsum amendment. Soil samples were collected 28 days after gypsum treatment. ns= not significant, *= significant at P<0.05.

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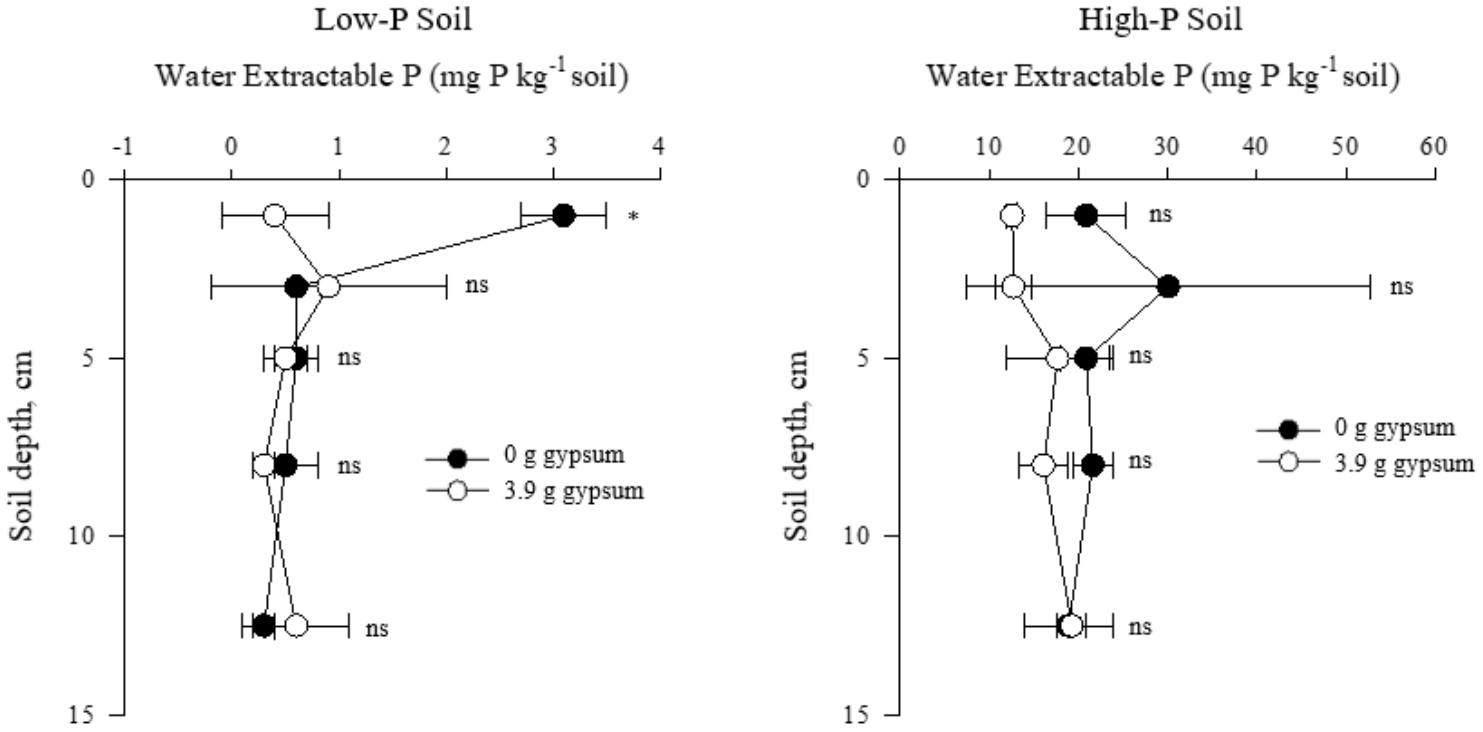


Figure 7. Depth distribution of water extractable P in untreated and gypsum-treated soil columns at the end of the second period of the experiment. Columns were amended with FGD-gypsum at an equivalent field rate of 5 Mg $ha^{-1}$ (3.9 g per column). Phosphorus fertilizer, in the form of a solution of $KH_2PO_4$ and at an equivalent field rate of 34 kg P $ha^{-1}$, was applied 28 days after gypsum amendment. Soil samples were collected 56 days after gypsum treatment. ns= not significant, *= significant at $P<0.05$.

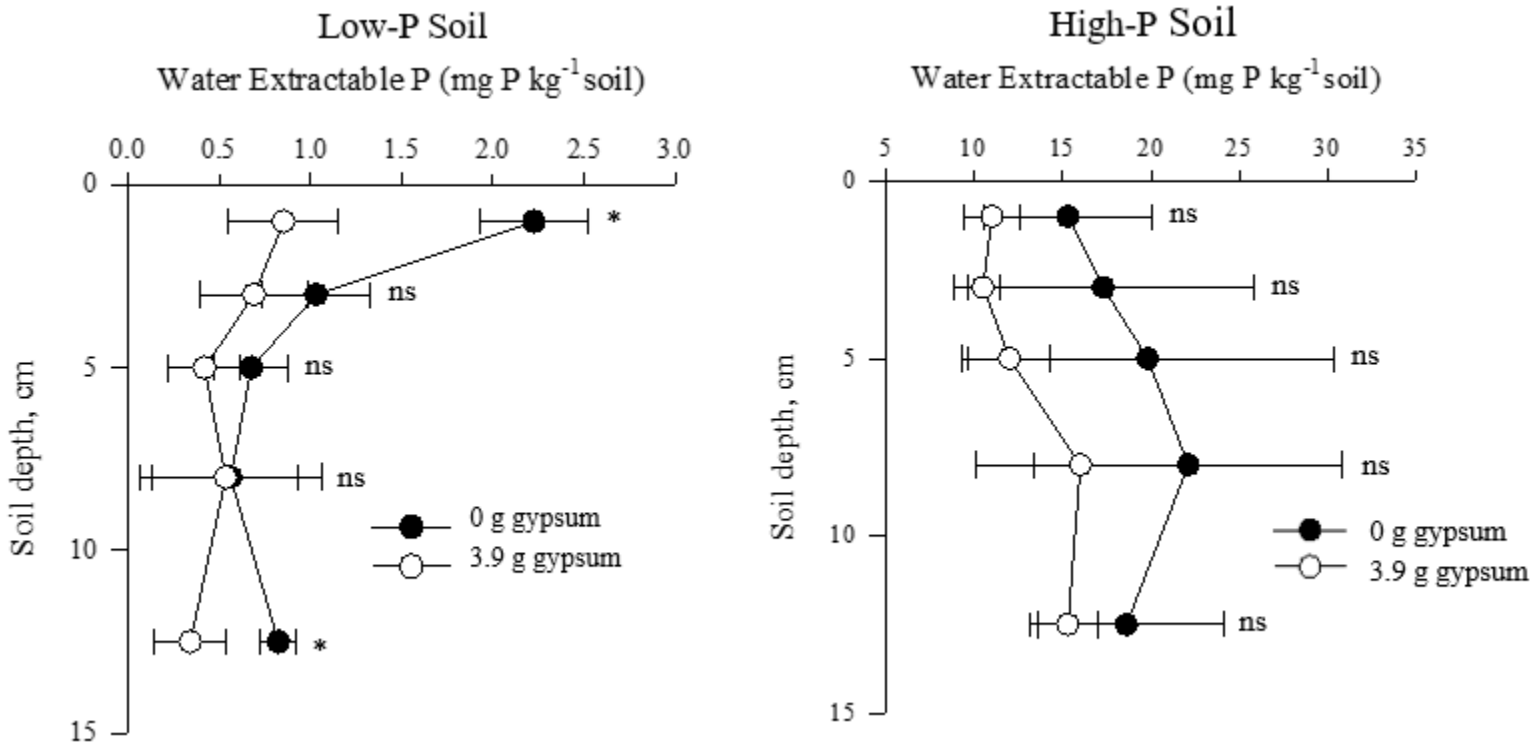
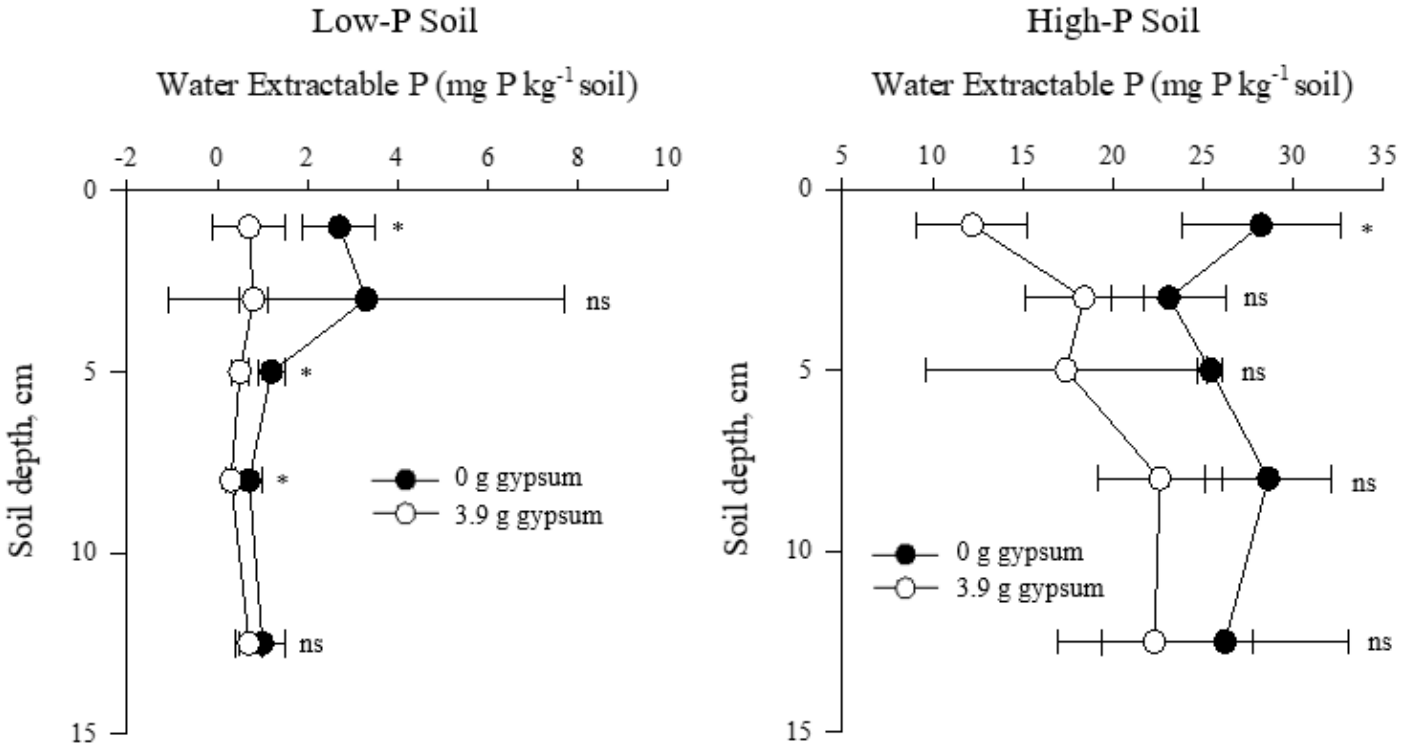


Figure 8. Depth distribution of water extractable P in untreated and gypsum-treated soil columns at the end of the third period of the experiment. Columns were amended with FGD-gypsum at an equivalent field rate of 5 Mg $ha^{-1}$ (3.9 g per column). Phosphorus fertilizer, in the form of a solution of $KH_2PO_4$ and at an equivalent field rate of 34 kg P $ha^{-1}$, was applied 56 days after gypsum amendment. Soil samples were collected 84 days after gypsum treatment. ns= not significant, *= significant at $P<0.05$.



3.7. Olsen-P in gypsum-treated soils

Regardless of soil type and collection period, none of the experimental factors (gypsum amendment, timing of phosphorus fertilizer application) had a statistically significant effect on Olsen-P (Table 13). Generally, untreated soil columns had slightly lower Olsen-P concentration than the gypsum-treated columns during the first and second collection period. There was little difference between gypsum-treated and untreated columns in terms of the depth distribution of Olsen-P, especially during the first and second collection periods (Fig. 9-10). However, during the third period, evidence of some differentiation began to emerge in the low-P soil (but not in the high-P soil). Significantly ($p<0.05$) lower concentration of Olsen-P was measured at 2-4 cm and 6-10 cm depth in the gypsum-treated than in the untreated columns (Fig. 11). Across the 0-10 cm layer in the low-P soil, Olsen-P averaged respectively 30.1 and 40.7 mg P $kg^{-1}$ soil in treated and untreated columns, indicating a 26% reduction in Olsen-P at the end of the third period.

Table 12. Depth-averaged concentration of Olsen-P (mg P kg-1 soil) in untreated and gypsum-treated soil columns as related to the time gap between gypsum amendment and fertilizer P application. Within a row for sampling time and for a given soil type, values followed by different letters are significantly different at P<0.05.

| Soil sampling, days | Time gap between Gypsum and P fertilizer addition, days | Untreated | Gypsum-treated | Untreated | Gypsum-treated |
|---|---|---|---|---|---|
| | | Low-P soil | | High-P soil | |
| 28 | 2 | 27.63a ±6.9 | 37.5b ±10.4 | 83.1a ±9.40 | 89.6a±17.77 |
| 56 | 30 | 32.4a ±3.74 | 34.3a ±6.35 | 127.9a ±13.43 | 137.2a ±23.77 |
| 84 | 54 | 39.6a ±6.96 | 30.4b ±6.11 | 164.0a ±8.56 | 187.4a ±10.71 |

Table 13. ANOVA results for the effects of gypsum treatment and timing of phosphorus fertilizer application on Olsen-P of soil collected from the columns. Results are presented by each soil type (high-P and low-P) and by each depth from which the soil was collected (0-2 cm, 2-4 cm, 4-6 cm, 6-10 cm, and 10-15 cm). ns indicates no significance.

| Class Variables | df | Low-P soil Olsen-P | | | | | High-P soil Olsen-P | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0-2 cm | 2-4 cm | 4-6 cm | 6-10 cm | 10-15 cm | 0-2 cm | 2-4 cm | 4-6 cm | 6-10 cm | 10-15 cm |
| Gypsum | 1 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| Time | 2 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| Gypsum X Time | 2 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns |

Figure 9. Depth distribution of bicarbonate-extractable P (Olsen-P) in untreated and gypsum-treated soil columns at the end of the first period of the experiment. Columns were amended with FGD-gypsum at an equivalent field rate of 5 Mg $ha^{-1}$ (3.9 g per column). Phosphorus fertilizer, in the form of a solution of $KH_2PO_4$ and at an equivalent field rate of 34 kg P $ha^{-1}$, was applied 2 days after gypsum amendment. Soil samples were collected 28 days after gypsum treatment. ns= not significant, *= significant at P<0.05.

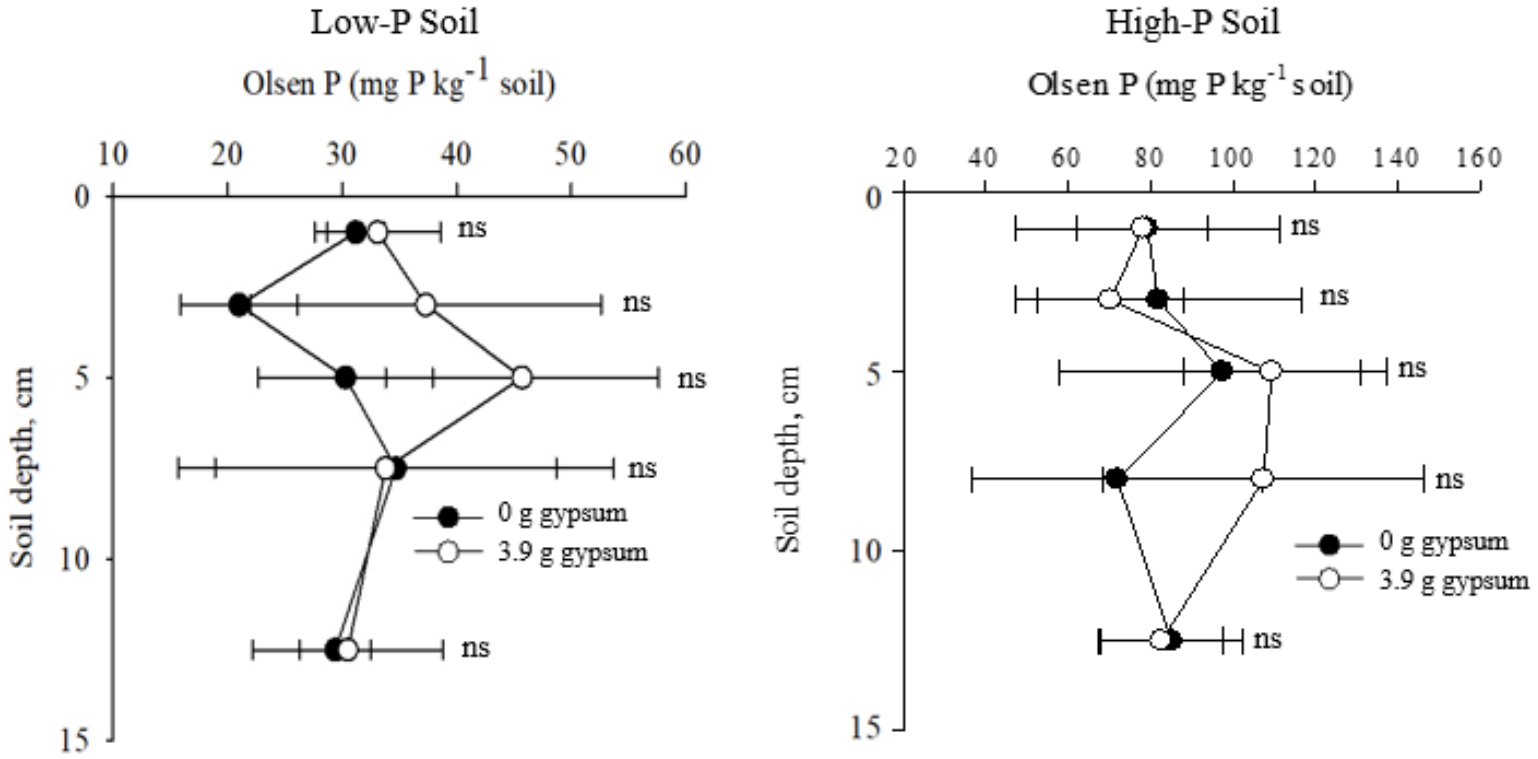


Figure 10. Depth distribution of bicarbonate-extractable P (Olsen-P) in untreated and gypsum-treated soil columns at the end of the second period of the experiment. Columns were amended with FGD-gypsum at an equivalent field rate of 5 Mg $ha^{-1}$ (3.9 g per column). Phosphorus fertilizer, in the form of a solution of $KH_2PO_4$ and at an equivalent field rate of 34 kg P $ha^{-1}$, was applied 28 days after gypsum amendment. Soil samples were collected 56 days after gypsum treatment. ns= not significant, *= significant at P<0. 05.

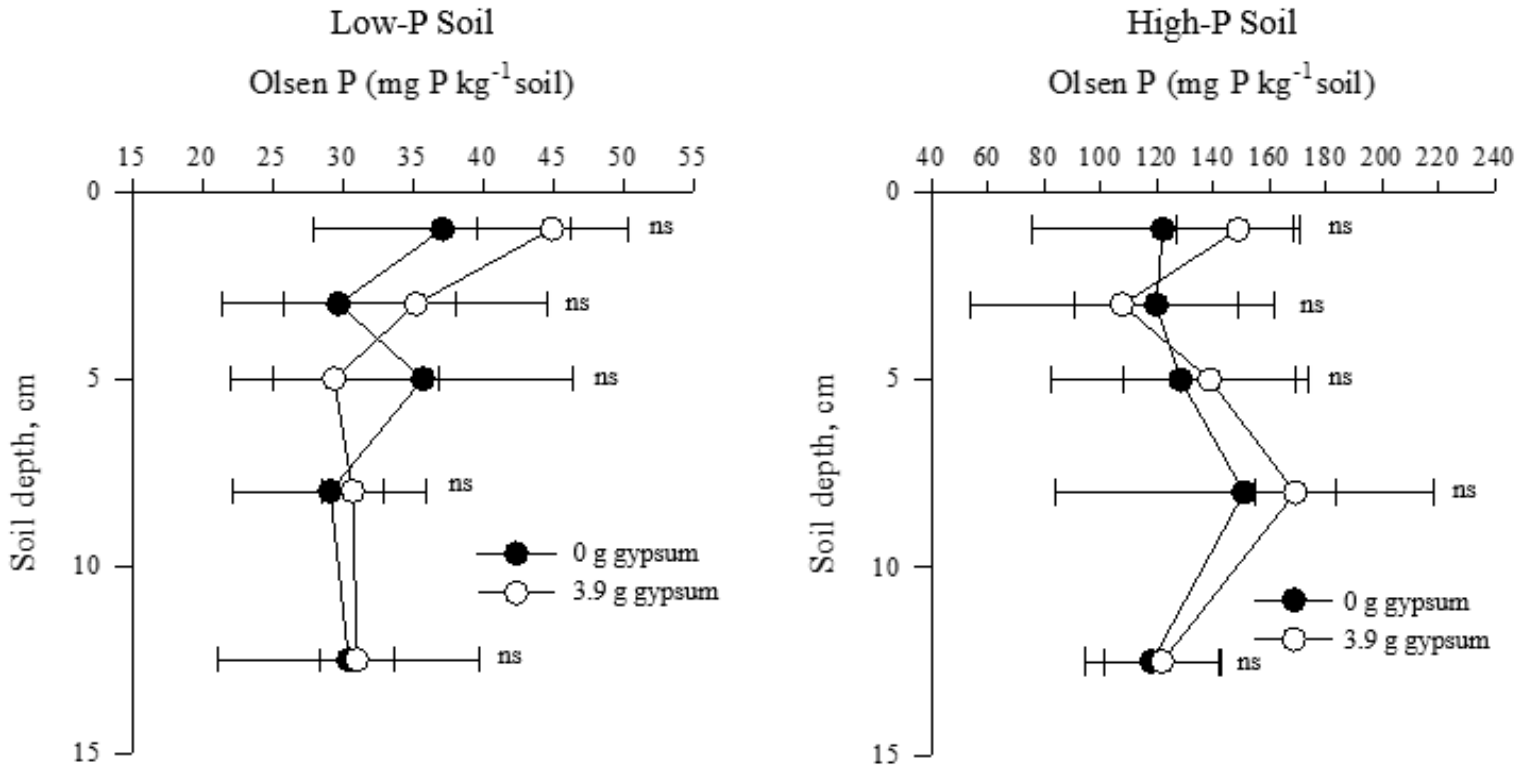
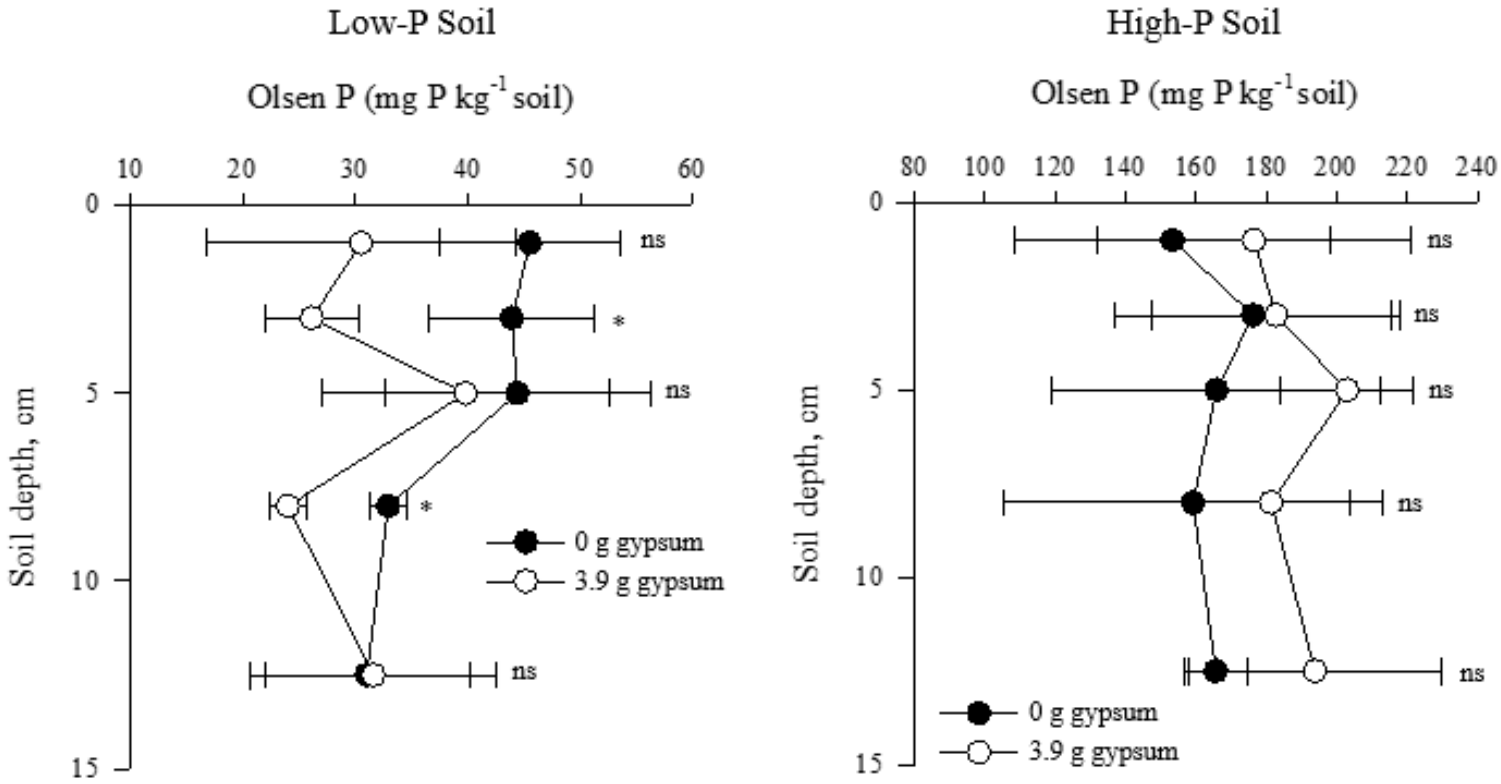


Figure 11. Depth distribution of bicarbonate-extractable P (Olsen-P) in untreated and gypsum-treated soil columns at the end of the third period of the experiment. Columns were amended with FGD-gypsum at an equivalent field rate of 5 Mg $ha^{-1}$ (3.9 g per column). Phosphorus fertilizer, in the form of a solution of $KH_2PO_4$ and at an equivalent field rate of 34 kg P $ha^{-1}$, was applied 56 days after gypsum amendment. Soil samples were collected 84 days after gypsum treatment. ns= not significant, *= significant at $P<0.05$.



# IV. DISCUSSION

The linkage between phosphorus fertilization of agricultural soils and degradation of water quality in agricultural drainage basins is well established. Various amendments have been proposed to improve phosphorus retention in soils and reduce off-field P export to surface water bodies. Although numerous studies have demonstrated the effectiveness of gypsum for that purpose, many questions remain regarding the impact of soil P status and timing of soil amendment on gypsum treatment effectiveness. This study sought to investigate these practical questions, and to understand potential shifts in plant available phosphorus as a result of soil amendment with gypsum. Results showed marked effects of gypsum treatment on soil water retention and water-extractable P.

## 4.1. Phosphorus loading reductions with gypsum treatment in relation to soil type

As described previously, at the start of the experiment soil columns were saturated by capillary action, allowed to drain, and then were watered every other day. Compared to the untreated columns, it took several more days (~4-6 days) for the gypsum-treated columns to produce measurable amounts of leachate. Overall, during the first portion of the experiment, leachate volume produced by the untreated columns was higher (24% in low-P and 14% in high-P soils) than in the gypsum-treated columns. Because of the added $Ca^{2+}$, gypsum is known to increase the water holding capacity of soils through flocculation of clay particles and improved soil aggregation (Fisher, 2011), and its effect on leachate volume is consistent with that understanding. That observation is critically important and suggests that, in a typical tile-drained agricultural field, gypsum application could lead to reduction in tile drain water discharge. The leaching of

P from soils is an important component of phosphorus export, particularly in dissolved form. The load of phosphorus exported from an agricultural field is the product of both phosphorus concentration and water discharge. Therefore, although the gypsum treatment may not always result in lower phosphorus concentration, the treatment could still have an impact on phosphorus loading through reduction in the volume of water transported. In fact, the temporal trend in leachate volume and phosphorus concentration in leachate suggests an intriguing dynamic between these two variables. For example, during the first period of the experiment, leachate volume was much less in gypsum-treated columns, but leachate P level remained largely unaffected by the gypsum treatment. In contrast, during the second and third periods, leachate volume became similar or higher in the treated columns, ortho-P and total-P concentrations were generally lower in leachate from the gypsum-treated columns. For the low-P soil, the average phosphorus load per sampling occasion (leachate volume multiplied by phosphorus concentration) was respectively 1.1 vs 1.6 μg ortho-P and 11.16 vs 11.24 μg TP in the untreated and gypsum-treated columns, suggesting no reduction in P load. In contrast, in the high-P soil, respective phosphorus loads were on overage 2.5 vs 1.6 μg ortho-P and 14.6 vs 13.5 μg TP in the untreated and gypsum-treated columns, suggesting a 7.5% reduction in TP and a 36% reduction in ortho-P with gypsum amendment. It is unclear why the gypsum treatment had limited to no effect on phosphorus loading in the low-P soil. The concentration of $SO_4^{-2}$ in leachate from the untreated columns was nearly 4 times higher in the low-P than in the high-P soils (172 vs 45 mg $SO_4^{-2}$ mL-1, respectively), suggesting an inherently high concentration of $SO_4^{-2}$ in this soil's solution. The low-P soil was collected from a field that periodically received S addition in the form of Thiosol (12.8 kg ha-1), a practice

thought to improve phosphorus uptake by growing corn crops but may have resulted in S enrichment over the years. Sorption onto solid surface is one of the well-known mechanisms via which gypsum regulates phosphorus mobility, and therefore increased competition between negatively-charged $SO_4^{-2}$ and $PO_4^{-3}$ for biding sites may have led to low retention of ortho-P (Geelhoed *et al*., 1997). Addition of $SO_4^{-2}$ with gypsum would further amplify the competition. Therefore, although limited effect of gypsum on phosphorus mobility was found in the low-P soil used in the present study, it is important to caution against generalization of that result because most low-P soils are not likely to be similarly enriched in $SO_4^{-2}$ .

In addition to sorption, phosphate precipitation as Ca-P minerals is another process most often invoked to explain the impact of gypsum treatment on phosphorus mobility in agricultural soils. Research has shown that humic acids can impede the formation of Ca-P crystals through occupation of developing crystal surface (Cao *et al*. 2007). It appears however that interference of organic matter on Ca-P formation and crystallization did not play a role because the gypsum treatment was most effective in the organic matter-rich soil.

## 4.2. Gypsum effectiveness and time gap since application

Amendment of agricultural of soils with gypsum has been recommend as a management practice to mitigate phosphorus export. Existing literature has mostly focused on defining appropriate gypsum application rates, but information about the most appropriate time for gypsum application has seldom been considered. This question is

important as some farmers make phosphorus fertilizer application during the non-growing season (after fall harvest, before spring thaw) in order to minimize the number of field operations to complete right before spring planting. The present study was designed to investigate the effect of time gap (2, 28 or 56 days) between gypsum and fertilizer application on the effectiveness of the gypsum treatment. During the first 24 days (and the second period in the high-P soil) of the experiment, the gypsum treatment resulted in lower leachate volume irrespective of soil type. However, as noted above, when assessment is based on either phosphorus concentration or phosphorus load, significant effects of gypsum were only recorded in the high-P soil. In that soil, ortho-P load reduction was -18%, 45% and 31% during the first, second and third periods, respectively. In regard to TP, load reduction was -25%, 13.4% and 19% during these periods. In other words, application of gypsum during the dormant season should not diminish its effectiveness even with a 2-month gap before phosphorus fertilizer application is made at the beginning of the next growing season.

A key question this study sought to answer is how long does the effect of gypsum amendment on soil phosphorus mobility last? More specifically, is the gypsum treatment as effective if phosphorus fertilizer is applied immediately with minimum lag time or after a 2-month time gap between these two operations. In an experiment involving gypsum amendment of experimental plots receiving poultry liter, Watts and Torbert (2009) noted that gypsum treatment resulted in a 32-40% reduction in ortho-P export in surface runoff. That response was short-lived, however; one month later the gypsum effect had vanished, and ortho-P concentration (3.1-3.3 mg $L^{-1}$) was similar in runoff from gypsum-treated and untreated plots. In contrast, Uusitalo *et al*. (2012) observed

significant effect of gypsum amendment on the concentration of ortho-P in percolation water up to 7 months after treatment initiation. Subsequent measurements into the third year of the experiment showed lower, although not significantly different, concentration of ortho-P in percolation water from gypsum-treated than untreated soils. Results of the present study are somewhere between these two extremes and suggest the duration of gypsum treatment could vary depending whether the focus is phosphorus export via surface runoff or via percolation water.

Due to its high solubility, rapid dissolution of gypsum likely takes place resulting in increased concentration of calcium ($Ca^{2+}$) and $SO_4^{-2}$ in soil solution. As a negatively charged chemical species, $SO_4^{-2}$ moves readily in infiltration water. Elevated concentrations of sulfate in leachate from the gypsum-treated columns are indicative of the rapid dissolution of gypsum and $SO_4^{-2}$ transport. The amount of $SO_4^{-2}$ in the rainwater used was relatively low (8.5 mg $L^{-1}$), and therefore rainwater could not account for differences in $SO_4^{-2}$ among treatments. It also appears that the mass of gypsum applied did not entirely or immediately dissolve because of the progressive increase in $SO_4^{-2}$ concentration in leachate even during the third collection period. Thus, at the applied rate, gypsum has the potential to affect phosphorus chemistry in soil for several months. It should be noted that, at the filed-scale level, the duration of gypsum treatment effect could be shorter if the area were to receive intense rainfall. The high solubility of gypsum also makes its susceptible to loss via surface runoff if application occurs immediately prior to a runoff-generating precipitation event.

Depending on $PO_4^{-3}$ activity in soil solution, this could promote the formation of Ca-P minerals of varying solubility (dicalcium phosphate, octacalcium phosphate,

apatite). Calcium ions released can also participate in the flocculation clay particles and soil aggregation. This may help explain the greater water retention (lower leachate volume) observed during the first period of the experiment. Initially, it is likely that the gypsum improved the soil structure, causing more of the water to remain in the soil. At the field-scale level, this observation would translate into lower volume of surface runoff, an important pathway for excess phosphorus running off agricultural fields into nearby waterways. However, with improved soil aggregation comes increased rate of water infiltration which allows water to saturate the soil profile to greater depths (Chen and Dick, 2011). In a field setting, this would mean more water is transported through the soil and less is exported through surface runoff. This interpretation is consistent with an earlier report of increased volume of subsurface drainage and decreased surface runoff with gypsum application (King *et al*., 2016). It is also in agreement with the observation of progressive increase of $SO_4^{-2}$ in columns leachate. As a neutral salt, gypsum is not expected to affect leachate pH and, consistent with that expectation, leachate pH was largely similar between treated and untreated columns. Nonetheless, leachate pH increased progressively during the course of the experiment and that increase was slightly greater in the gypsum-treated columns suggesting perhaps displacement of $Mg^{+2}$ and $OH^-$ ions (although these elements were not measured) over time.

### 4.3. Plant available phosphorus following gypsum treatment

Another question the study sought to explore was to determine whether excess of $Ca^{+2}$ in soil solution following gypsum treatment could negatively impact phosphorus

uptake by vegetation. To address that question, two indices of phosphorus availability were used: water-extractable and bicarbonate-extractable P (or Olsen-P).

The Olsen-P method is the most common extraction procedure to assess the pool of plant available phosphorus in soils developed from calcareous parent materials. Olsen-P was found to be similar to untreated and gypsum-treated soils at almost all soil depths, and regardless of soil P status and the time gap between gypsum and fertilizer phosphorus application. The bicarbonate extracting solution (pH: 8.5) used in that method is thought to promote Ca-phosphate dissolution. The method was likely not sufficiently selective in regard to the Ca-P minerals it dissolves and therefore provides no insight into alteration in soil P chemistry induced by the addition of gypsum. There may have been conversion of more labile P to Olsen-P, but the duration of the experiment may have been too short or the magnitude of these shifts was too small to be detected (except in the high-P soil during the second and third periods when Olsen-P was significantly higher in the gypsum-treated). Previous studies have also reported no effect of gypsum treatment on plant available P, including Olsen-P (Stout *et al*., 2003; Brauer *et al*., 2005; and Kost *et al*., 2004). It should be noted measured Olsen-P was still within a range (27-39 mg P $kg^{-1}$ in low-P soil; 65-92 mg P $kg^{-1}$ in high-P soil) considered adequate or more than sufficient to sustain the growth of most crops.

The effect of gypsum treatment on water extractable P was one of the most important and consistent findings of the study. Water extractable P is a common form of phosphorus in runoff and a major cause of impaired waterways. It is immediately available for biological productivity which can lead to algal blooms (Brauer, *et al*., 2005; Bryant, *et al*., 2012; Favaretto, *et al*., 2012; Stout, *et al*., 2003; and Watts and Torbet,

2009). Almost always, regardless of the soil type and period of the experiment, the gypsum-treated soil had lower level water-extractable P. Past studies have shown that gypsum treatment can reduce the pool of water-extractable P in soils, specially soil containing high amounts of phosphorus (Stout *et al*. 2003; Brauer *et al*., 2005; and Kost *et al*., 2004). Possible mechanisms for the reduction in water-extractable P likely involves precipitation reactions between dissolved phosphate anion and $Ca^{2+}$ ions released by the dissolution of gypsum (Sindelar and Wolkowski, 2019). Excess $Ca^{2+}$ and alkaline soil conditions have been found to be favorable to precipitation of P-bearing minerals (McLaughlin *et al*, 2011). The probability of such reactions increases when activity of the reactants in solution is higher, explaining why the impact of gypsum treatment on water-extractable P was more pronounced in the high-P soil than in the low-P soil. Initially-formed Ca-P precipitates may still be susceptible to dissolution and release of ortho-P into soil solution. However, that possibility is less likely, and lower solubility minerals begin to form. These considerations would explain why the gypsum-induced decrease in water-extractable P was not statistically significant during the first collection period (2-24 days), but over a longer period of time the effect became more visible and extended to the deeper soil layers. Secondary Ca-P minerals likely to form include relatively soluble dicalcium-phosphate followed by octacalcium phosphate. Under the right conditions (alkaline pH) and with enough time, hydroxyapatite will precipitate (McLaughlin *et al*, 2011; Kordlaghari and Rowell, 2006).

# V. CONCLUSION

## 5.1. Changes in leachate volume and phosphorus concentration with gypsum treatment

Phosphorus is a critical plant nutrient and essential for growth, but excessive availability of phosphorus poses a risk to nearby surface waters and can potentially lead to eutrophication. This is especially concerning in intensive agricultural landscapes where synthetic phosphorus fertilizer and other phosphorus-rich organic fertilizers such as manure are continuously used. Application of gypsum to soils with high phosphorus content, including manure-treated fields, can aid in the control of phosphorus export from agricultural fields. The decrease in the amount of water-extractable P with gypsum application was an important finding since this phosphorus pool is positively correlated with phosphorus export from soil. Because of its high mobility, controlling the water extractable phosphorus pool is crucial to mitigate phosphorus loading and associated environmental concerns especially in tile-drained agricultural fields.

Studies have shown that gypsum has an effect of soil structure and water holding capacity. This study results have shown that those benefits are not immediate upon gypsum application but begin to manifest after the 28-day mark. Initially, leachate volume was lower in the gypsum-treated columns. Overtime, the gypsum treatment likely resulted in improved the soil structure, allowing for flocculation of clay particles and creation of pore space for water to move downward (Chen and Dick, 2001). With the understanding that surface soil sealing could enhance phosphorus loss via surface runoff, this effect is beneficial especially in soils susceptible to surface crusting during dry periods. The present study was not designed to investigate runoff phosphorus loss, but

positive effect of gypsum on this phosphorus loss mechanism has widely been reported (Favaretto, *et al.*, 2006; Watts and Torbet, 2009).

This study has provided useful information that would help determine the agriculture settings where gypsum treatments would be most beneficial. For the low-P soil, the gypsum treatment did not yield a significant reduction in leachate ortho-P, and the reason for these results remains to be elucidated. However, fields that have a high phosphorus content, especially those that have a history of manure use, would likely benefit from the application of gypsum. Additionally, results have suggested that it would be best to apply gypsum after fall harvest as his would allow for ample time for the added calcium (from gypsum) to fully penetrate the soil matrix and limit the mobility of water soluble phosphorus when fertilizer application is made prior to spring planting.

## 5.2. Future Studies

Results of this study have shown that gypsum application lowers the levels of water available phosphorus in agricultural soils and has a greater effect on phosphorus mobility when it is applied to high-P soils than low-P soils. Major factors that influence availability of phosphorus in soil include clay content, soil mineralogy, soil pH, and organic matter content. This study did not directly investigate the of presence of organic matter, but it may have played a role in controlling phosphorus availability. In addition to water extractable P and Olsen-P, a more in-depth examination of the various forms of phosphorus in the gypsum-treated soils would have provided additional insights into the temporal evolution of different Ca-P minerals in the gypsum-treated soils. The use of x-

ray diffraction would have provided a closer look of soil mineralogy and allowed for a closer examination of the effect of added $Ca^{2+}$ cations on the formation of P-bearing minerals. Due to the nature of the reactions likely to take place, studies of much longer duration would have provided more insight into the timeline of the precipitation of Ca-P bearing minerals in soils with added gypsum.

Finally, as with most greenhouse experiments, this study has some inherent limitations. The dynamics of phosphorus movement in reconstructed soil columns may not accurately reflect field conditions where phosphorus leaching is likely controlled by rainfall events and phosphorus uptake by growing vegetation – conditions that were absent in this study. Therefore, field-scale investigations should be conducted to determine the effect of application timing on the beneficial effect of gypsum.

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CURRICULUM VITAE

**Kristiana Cox**

## Education

December 2020 — Master of Science in Geology, Indiana University, earned at Indiana University Purdue University – Indianapolis
Master's Thesis: "Effect of Soil Type and Fertilizer Application Timing on Phosphorus Leaching from Gypsum-Treated Agriculture Soils"

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May 2014 — Bachelor of Science
Ball State University, Muncie, IN
Major: Geology
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Dean's List: Spring 2011-Spring 2014
Cum Laude

## Academic Experience

### Teaching Experience

-IUPUI Teaching Assistant: Physical Geology Lab
-Fall 2014 - Spring 2016
-IUPUI Teaching Assistant: Environmental Geology Lab
-Spring 2015 - Spring 2016
-Ball State University Teaching Assistant: Introduction to Geology Lab
-Spring 2012 - Fall 2013

### Lab Experience

-IUPUI Soils Lab
-Prepare and run leachate water samples on Aquachem Konelab analyzer

-Ball State University Immersive Learning
-Work with and teach Journalism students to collect and analyze water samples from Buck Creek in Delaware County, Indiana.

## Work Experience

Hydrogeologist — September 2016-Present

-Indiana Department of Natural Resources, Division of Water
-Create bedrock and unconsolidated aquifer potentiometric surface maps for internet publication by contouring static water levels from selected Indiana well records
-Collected information and publish Monthly Water Resource Summary each month on IDNR's Water webpage
-Review permit applications and water well records to write Lake Vulnerability reports for construction projects in waterways
-Attend monthly Indiana Water Monitoring Council- Groundwater Focus Committee meetings as a representative of IDNR-Division of Water

GIS Technician — July 2016-September 2016

-Indiana Department of Natural Resources, Division of Water
-Assist Resource Assessment Section staff in preparation of potentiometric surface maps for internet publication

Ball State University/Geothermal Field Assistant — September 2012-May 2013

-Responsible in assisting graduate student in the geothermal field for thesis research
-Take temperature profiles and recharge times of wells drilled through the geothermal field
-Collect water samples from each well and take geochemical readings
-Assist with calibrating geochemical measuring devices

Ball State University/Geothermal Lab Assistant — January 2011-May 2011

-Logged and described the cuttings bagged during the drilling of wells in the geothermal field

## Professional Presentation

-Geological Society of America Southeast: A Water Quality Assessment of Buck Creek in East Central Indiana (April 2014)

## Awards

| | |
|---|---|
| -Ball State University Cum Laude | May 2014 |
| -Ball State University Excellence in Field Geology | February 2014 |
| -Ball State University Samuelson Outstanding Senior Award | February 2014 |
| -Ball State University Kane Outstanding Junior Award | February 2013 |
| -Ball State University Dean's List | Spring 2011-Spring 2014 |

## Professional Memberships

| | |
|---|---|
| -Indiana Water Monitoring Council Committee | 2016-Present |
| -Indiana Water Resources Association | 2017-Present |
| -Geological Society of America | 2012 - 2016 |
| -American Institute of Professional Geologists | 2012 - 2016 |